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New method for arsenic compounds elimination from naturally contaminated drinking water systems

Ph.D. Thesis

Submitted by

Krzysztof Piotr Kowalski

**To the Faculty of Engineering and Science, Aalborg University
For the Degree of Doctor of Philosophy**

Supervisor: Professor mso Erik G. Sogaard

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This thesis has been submitted for assessment in partial fulfillment of the PhD degree. The thesis is based on the submitted or published scientific papers which are listed in the chapter “List of publications”. Parts of the papers are used directly or indirectly in the extended summary of the thesis. Part of the assessment, co-author statements have been made available to the assessment committee and are also available at the Faculty. The thesis is not in its present form acceptable for open publication but only in limited and closed circulation as copyright may not yet be ensured.

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Paper 4 (submitted):

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3. Kowalski K., Søgaard E.G., 2012: Simple Water Treatment System for Heavy Metals Removal with Usage of the Zero-Valent Iron - Pilot Test Results, Oral presentation at Singapore International Water Week (SIWW) 2012, Singapore, July 2012
4. Kowalski K., Søgaard E.G., 2012: Removal of the arsenic from contaminated groundwater with use of the new generation of MicroDrop Aqua system. Poster for 6th IWA International Conference for Young Water Professionals: Conference Proceedings. July 2012
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 - a. Kowalski K. and Madsen H.T., Søgaard E.G.: Integration of sand and membrane filtration systems for iron and pesticide removal without chemical addition
 - b. Kowalski K., Søgaard E.G. Comparison of a sand and membrane filtration unit for drinking water production –focus on the arsenic removal;
6. Kowalski K., Søgaard E.G., 2013: Comparison of the new iron dosage methods for drinking water production. Poster presented at Electrochemical Science and Technology Conference 2013, Ringsted, Denmark, October 2013
7. Kowalski K., Søgaard E.G., 2013: Improved Aeration Process - Catalytic Role Of The Iron Oxides In Arsenic Oxidation And Coprecipitation, Oral presentation at Amsterdam International Water Week (AIWW) 2013, November 2013

Dedication

*This dissertation is lovingly dedicated to my wife, Anna.
This thesis would not have been possible to write without your support,
encouragement, and constant love.*

Preface and acknowledgement

The Ph.D. project was conducted within the field of water treatment technology with the main focus on arsenic compounds removal for drinking water production. The project was carried out in the period January 2011 to December 2013 under the Industrial Ph.D. program and the work was partly funded by MicroDrop Aqua ApS and the Danish Agency of Science, Technology and Innovation. The Industrial Ph.D. program enabled me to confront my academic knowledge with water industry issues regarding groundwater treatment and implementation of technologies provided by the MicroDrop Aqua.

This all was done under supervision of Professor mso Erik G. Søgaard from Section of Chemical Engineering, Department of Biotechnology, Chemistry and Environmental Engineering, Aalborg University in Esbjerg. Therefore I would like to express my deepest thanks to him especially that this thesis is the culmination of a long period of our cooperation that started during my Master of Science program at AAUE. I want to thank for his supervising, mentoring and support in this career path.

Numerous people over the years have helped me get here, so there are many people I need to thank. My sincere thanks go to Kasia R. Arturi, Henrik T. Madsen and Jimoh I. Adetunji, not only for their scientific contributions and discussions, but also for nice time spent together. Moreover, many thanks to Adeel Sohal, Camilla and Miłosz Sønderby, Jens Muff, Heidi Thomsen, Pavel Spirov, Morten Simonsen, Rudi Nielsen and the others current and former members from the CICHEM research group for collaboration and social activities that made my stay at the university enjoyable. I would like to specially thank the laboratory staff: Dorte, Linda, Vivi and Morten for their advices and analytical work. Moreover, the help of Henry Enevoldsen is much appreciated.

I would also like to acknowledge the support that I obtained during my work at the MicroDrop Aqua from my colleagues and the management. Moreover I would like to thank to Jørgen C. Blandfort for sharing his expertise about the Danish way of water treatment.

Finally my gratitude goes to my family, especially my Mum and Dad whose love and support was encouraging and invaluable. As well thanks to my friends, without you I would not be able to take my mind off the project. And most of all for my loving, supportive, encouraging, and patient wife Anna whose faithful support during the final stages of this Ph.D. is so appreciated. Thank you.

Esbjerg, January 2014

Krzysztof P. Kowalski

Abstract

This Ph.D. dissertation dealt with iron based techniques methods of arsenic removal technologies for drinking water production. The dissertation focused on evaluation of a novel techniques for iron dosage and dissolved oxygen supplementation, which were offered by MicroDrop Aqua (MDA), together with different separation methods.

The thesis is organized in a way to guide the reader through a conventional groundwater treatment process, i.e. firstly iron ions addition followed by the aeration unit and separation techniques. Each unit process, and especially its novel form, is the subject of different articles that demonstrate its implementation at different scale, pilot or small waterworks. Hence, instead of a conventional iron dosage system, i.e. as a salt, an iron electro dissolution process or zero-valent iron was implemented and the aeration process was improved by application of a novel aeration tower. Additionally, studies about sand media and membrane filtration techniques to remove arsenic by help of its co-precipitation with iron were also performed. The roles of arsenic speciation, groundwater quality and possible mechanisms, involving physico-chemical or biological processes, during the arsenic treatment were highlighted. The results were confronted with a current knowledge about iron based methods for arsenic and other contaminants removal, which review was introduced for better understanding of issues that the novel techniques can face in the full scale treatment.

Paper 1 is about the electrolytic iron dissolution and efficient aeration procedure prior to sand filtration, which was introduced and investigated in a pilot scale plant and full scale waterworks in Denmark. Especially the use of the system for 14 months revealed a relationship between the process conditions (flow and applied current) and arsenic removal efficiency. Moreover the long period of use also helped to determine a proper iron dosage and identify carbonate scale formation in the electrochemical process.

The purpose of Paper 2 was to study a treatment based on the zero-valent iron (ZVI), aeration with the MDA system and sand filtration that was monitored for a period of 45 month. It was found that in the applied configuration and conditions, ZVI was not able to remove arsenic solely, but it worked as a source of ferrous ions that enabled to co-precipitate arsenic and phosphates compounds in the sand filter. To achieve a required treatment efficiency the lag phase of about 6 months was necessary to develop bacteria in the sand media. The results also indicate that the phase might have been also needed to initiate iron ions release from elemental iron by help of microbial activity.

The aim of Paper 3 was to present advantages of arsenic oxidation in an aeration process in the presence of ferrihydrite surface that have been shown to adsorb arsenic simultaneously to its oxidation. In the pilot scale studies the adsorption of arsenite on ferrihydrite was found to be the main process occurring during the aeration. Moreover, it was found that the adsorption rate might have been limited by an excess of dissolved iron, due to competition between arsenic and iron compounds for adsorption sites on iron oxyhydroxide surface.

In the Paper 4 arsenic removal from groundwater by help of membrane processes, micro- and ultrafiltration, was evaluated and compared with sand media filtration. The results showed

that membrane filtrations were able to remove arsenic compounds in co-precipitation with iron compounds regardless of applied filtration conditions (TMP, Permeate flow). The comparison between membrane and sand media filtrations was based on the Fe/As ratio from fouled material and backwash samples. The ratio was affected by the arsenic speciation and the presence of phosphates and NOM, which were found to be responsible for hindering total As removal by help of iron precipitates. Moreover, the presence of NOM increased the fouling potential, which shall also be considered in the full scale treatment with use of membrane filtration.

Paper 5 presents pilot plant investigations of sand and membrane filtration (MF/UF/NF/LPRO) to treat groundwater polluted with pesticides. The results showed that simple treatment by use of aeration and the MDA-system together with sand filtration or MF/UF membranes, did not remove the pesticides. However, by reducing the content of key foulants, the techniques can be used as a pre-treatment for nano filtration and low pressure reverse osmosis that has proved to be capable of removing pesticides.

Abstrakt

Denne Ph.D. afhandling omhandler jernbaserede metoder til fjernelse af arsen fra drikkevand. Afhandlingen fokuserer på en evaluering af innovative metoder til dosering af jern og iltning, som blev udviklet af MicroDrop Aqua, og herunder forskellige separationsmetoder.

Rækkefølgen af emner i denne afhandling afspejler den konventionelle grundvandsbehandling, hvilket inkluderer tilsætning af opløst jern som bliver efterfulgt af iltning og forskellige separationsteknikker. Hver enhedsoperation bliver beskrevet i et separat artikel hvor forskellige teknikkers effektivitet (eller virkemåde) testes i laboratorieskala, pilotskala, og/eller på vandværker. De anvendte innovative teknikker for jern dosering omfatter elektrolytisk oxidation og opløsning eller anvendelse af nul valent jern (zero-valent iron, ZVI), mens iltning processen bliver effektiviseret vha. et innovativt iltningstårn. Derudover, bliver også copræcipitation af arsen ved udfældning af jern i sand filtre og separationsprocesser vha. membraner undersøgt.

I afhandlingen bliver rollen af oxidationstrinnet, grundvandets kvalitet, og mekanismer (fysisk-kemiske eller biologiske) for arsen udfældning fremhævet. De opnåede resultater bliver sammenholdt med viden om jern-baserede teknikker for fjernelse af både arsen og andre forurenende stoffer med det formål at øge forståelsen for problemer og udfordringer som de innovative teknikker kommer til at stå overfor i et fuld skala behandlingsanlæg.

Artikel 1 omhandler den elektrolytiske opløsning af jern og en effektiviseret iltning forud for sandfiltrering. Begge teknikker blev introduceret og undersøgt på et pilotskala anlæg og et vandværk vha. en række eksperimenter, som viste en sammenhæng mellem de anvendte procesbetingelser (vandgennemstrømning og påtrykte strøm) og effektivitet for arsen fjernelse. Dette blev fastlagt vha. 14 måneders overvågning af de involverede systemer, som også har været med at fastlægge den optimale dosering af jern, samt at identificere produkter for kedelsten dannelse i den elektrokemiske proces.

Formålet med Artikel 2 var at undersøge effektiviteten af en behandling baseret på ZVI, iltning og sandfiltrering som blev foretaget og overvåget i 45 måneder på et mindre vandværk i Danmark. Det blev konstateret, at ZVI i den anvendte konfiguration og med de pågældende betingelser ikke var i stand til at fjerne arsen. Til gengæld virkede systemet som en kilde til jernholdige ioner, og gjorde det muligt at copræcipitere arsen og fosfatforbindelser i sandfiltrene. Den ønskede effektivitet for processen kunne opnås efter 6 måneder med bakteriel vækst i sandfiltret. Resultaterne indikerer at dette tidsrum var nødvendig for at frigøre jern vha. mikrobiologisk aktivitet.

Formålet med Artikel 3 var at præsentere fordele ved arsen oxidation der involverer iltning ved tilstedeværelsen af et en ferrihydrit overflade, som adsorberer produkter fra reaktioner sideløbende med oxidationen af arsen. I undersøgelser foretaget på pilot skala anlægget viste absorption af arsenit på ferrihydrit overfladen sig at være hovedprocessen og ansvarlig for udfældning af As. Desuden blev det konstateret, at adsorptions hastigheden kunne have været begrænset af et overskud af opløst jern, som medførte en rivalisering mellem arsen og jernforbindelser til at komme til adsorption “sites” på FeOOH overfladen.

I artikel 4 blev fjernelse af arsen fra grundvand ved hjælp af mikro- og ultrafiltrering evalueret, og sammenlignet med sand filtrering metoden. Resultaterne viste, at membran filtreringen var i stand til at fjerne arsen forbindelser vha. copræcipitation med jernforbindelser uanset de anvendte filtreringsbetingelser (TMP, permeatstrøm). Sammenligningen mellem membran filtrering og sand filtrering er baseret på Fe/As -forholdet fra fouling aflejrings og backwashprøver. Værdien af Fe/As ratio var påvirket af arsen specieringen, tilstedeværelse af fosfater og organisk materiale. Alle disse faktorer forhindrede fjernelse af arsen igennem udfældning af jern. Desuden har tilstedeværelse af organiske forbindelse forøget potentialet for fouling, som skal overvejes nøje i et fuld skala anlæg.

Artikel 5 beskriver undersøgelser af membranfiltrering på et pilot skala (MF/ UF/ NF/ LPRO) anlæg til behandling af grundvand forurenet med pesticider. Resultaterne viste, at en simpel behandling med anvendelse af iltning og sandfiltrering eller MF / UF -membraner, ikke kan fjerne pesticider fra grundvand. Teknikken viste sig dog at være effektiv i at fjerne hovedkomponenter ansvarlige for fouling og derfor kan bruges som en form for forbehandling før nanofiltrering eller omvendt osmose. Begge teknikker er effektive mod pesticider i grundvand.

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1. Introduction

1.1. Background

Arsenic is a metalloid, which naturally occurs in the environment, but is proven to have negatively influence on a human health, and even in higher doses was used as a poison. An arsenic occurrence in drinking water has been proven to be responsible for many diseases in Bangladesh and India. Thus, it has been considered as one of the six world's worst pollution in 2010, in Blacksmith's Institute Report and situation in Bangladesh was described as “ the largest mass poisoning of a population in history...beyond accidents at Bhopal, India, in 1984, and Chernobyl, Ukraine, in 1986”(McCartor and Becker, 2010).

Therefore, the arsenic problem has been considered as one of the main issues within researches and authorities. And for the last 20 years a number of studies aiming finding a solution to this problem have increased significantly as a consequence of implementation of stricter drinking water quality guidelines (Figure 1).

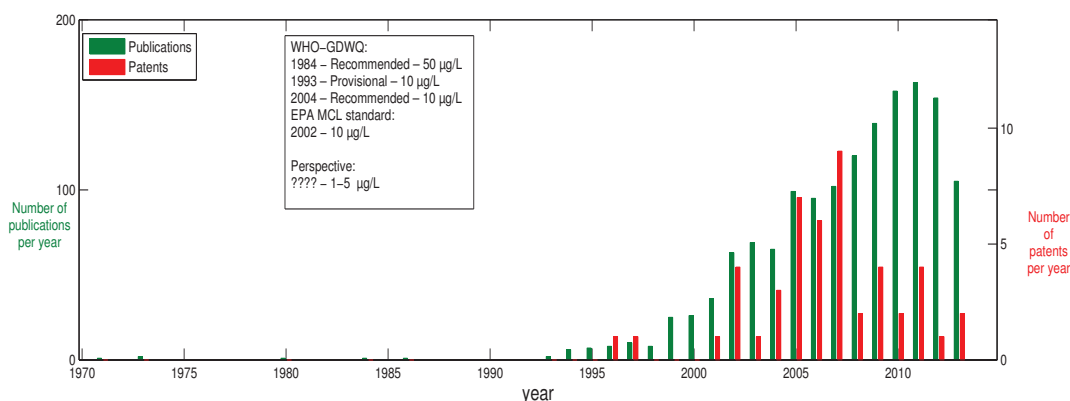


Figure 1 Number of publications and patents concerning arsenic removal for drinking water production as a response to decreasing allowance of As in drinking water by World Health Organization and U.S. Environmental Protection Agency (WHO-GDWQ - Guidelines for Drinking-water Quality, EPA-MCL – U.S. Environmental Protection Agency Maximum Contaminant Level)

However, any solutions for arsenic in drinking water have to consider socio-economic and technological aspects. It is still a major challenge in the developing countries, where a sustainable arsenic remediation technology is needed and there are calls for actions towards implementation of the technologies and engagement of different governmental and non-governmental organizations (Murcott, 2013; Sarkar et al., 2012). In the other situation are developed countries, where focus is made on producing water fulfilling the highest standards with help of energy efficient and environmental friendly methods. Moreover the treatment will have to face not only strict current drinking water standards, but also be adjustable to the future ones. Especially a discussion about further changes in potable water quality guidelines is ongoing due to consumer expectance and available technologies in Europe and North America (Halem et al., 2009).

The most frequently used conventional method for arsenic removal is based on precipitation/co-precipitation with alum or ferric chloride (Jain and Singh, 2012). However the Danish authorities have limiting possibilities for arsenic removal treatment from contaminated groundwater by prohibiting a range of techniques used for this purpose (Danish Ministry of the Environment, 2007). In 2012 30 permits were granted to apply advanced water treatment for arsenic removal, which includes addition of iron chloride, iron sulphate or adsorption filters with iron oxide (Villumsen, 2012). New improvements of the conventional method have been proposed by a Danish company, MicroDrop Aqua. The company has developed novel technologies of iron dosage and the aeration process that can be applied and incorporated into existing waterworks and they can be found within the MicroDrop Aqua patent portfolio:

- Method for removing contaminant trace species, especially arsenic, from water (Lebech, 2011);
- A method for producing potable water by enhanced removal of trace species contaminants (Guldager, 2012).

1.2. The research objectives and scope of investigation

The investigations of iron based techniques for groundwater treatment were the scope of the study, which focus on arsenic removal. Current knowledge about interactions between iron and arsenic compounds, mechanisms occurring and limitations is used to investigate elements behaviour in the implemented treatments. The investigations were not only limited to technologies provided by MicroDrop Aqua ApS, but also included in studies about separation techniques. The techniques that were in the scope of the study, i.e. iron dosage, aeration and separation techniques are presented on Figure 2.

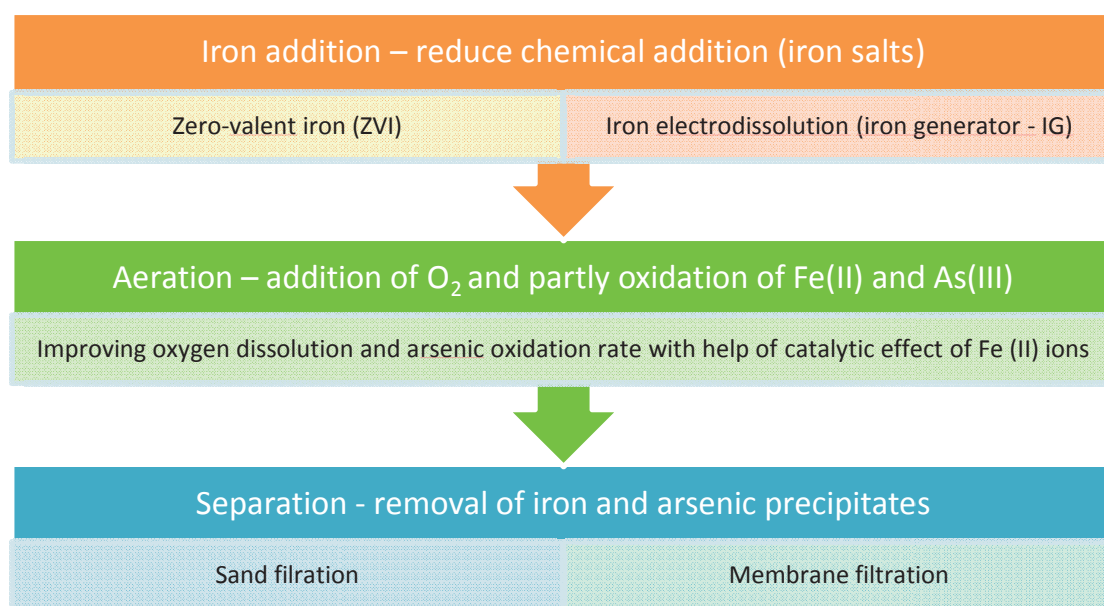


Figure 2 Conventional arsenic removal and their possible improvements

Description of the physico-chemical and possible biological processes occurring at different stage of the treatment was the overall purpose of the study. The project objectives were divided into 3 areas and include:

- Iron addition:
 - Investigation of iron ions release during application of zero-valent iron and iron electrodisolution applied in a full scale;
 - Role of biological processes during in spontaneous redox reactions on the elemental iron surface;
 - Identification of constrains related to water constituents that might limit iron ions release;
- Aeration:
 - Identification of chemical processes occurring during the aeration and in the presence of iron(III)-hydroxides, i.e. pseudo-Fenton reactions and adsorption/coprecipitation of arsenic compounds;
 - Investigations of the process effectiveness, regarding oxidation and coprecipitation of arsenite;
- Separation:
 - Investigations of mechanisms responsible for separation of iron and arsenic precipitates during sand media and ceramic membrane filtration;
 - Studies of required Fe dose and influence of organic and inorganic compounds on it.

Additionally, this work also studied treatment aiming the removal of pesticides from groundwater and the objective was an evaluation of applicability of the processes.

Achievement of this research was based on a review of current techniques of arsenic contaminated waters. With the current knowledge it was possible to understand the mechanisms of arsenic compounds oxidation and coprecipitation by help of iron ions and precipitates in full and pilot scale. The full scale treatments of the MicroDrop Aqua technologies were performed at Danish water waterworks for long periods of time enabling deeper understanding of the processes and their limitations (Figure 3).

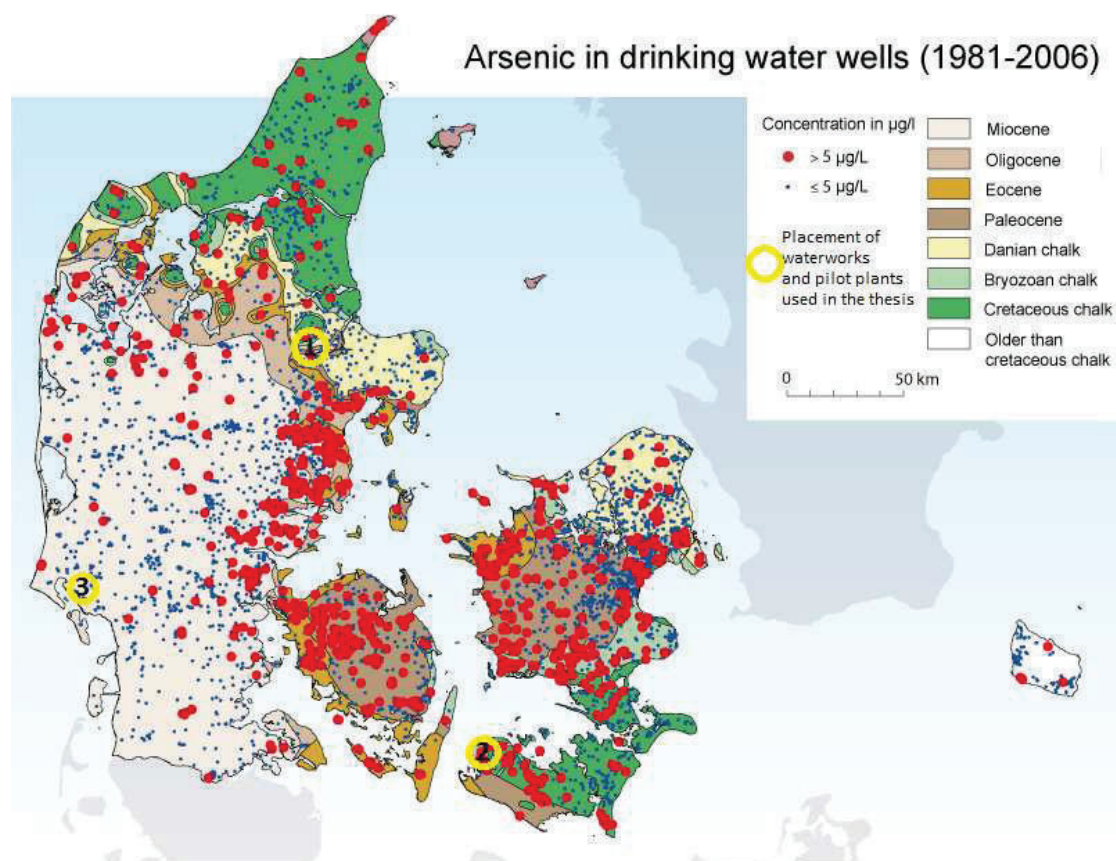


Figure 3 Arsenic occurrence in Danish groundwaters and placement of full and pilot plants presented in this study (1 – Bjergby Søndre waterworks; 2 – Utterslev Kastager waterworks; 3 – pilot plants at AAUE) (Modified from GEUS' Viden om Grundvand. Copyright: Geological Survey of Denmark and Greenland (GEUS, 2004))

1.3. Thesis structure and content

The present thesis is organized as articles aiming to present different aspects of the novel treatment preceded by an introduction part about to arsenic compounds and their effect on human health (Chapter 2) and, foremost, the review about methods for arsenic removal (Chapter 3), providing information about general technologies of arsenic removal, but the attention was put on iron based techniques. The articles, 2 acceptor and 2 submitted and 1 published, are in an order that helps in guiding through the process of arsenic removal, i.e. from iron dosing, aeration to separation techniques, as presented on Figure 2. The findings about the novel techniques provided by the MicroDrop Aqua are highlighted and summarized in Chapter 4, which is followed by conclusions provided in the last chapter (Chapter 5).

2. Arsenic occurrence and effects

2.1. Arsenic species

The most common natural arsenic compounds are arsenite and arsenate. The first one, with As oxidation state +3, can be found in a non-ionised form (H_3AsO_3) in pH range 0-9. Only in basic conditions ($\text{pH} > 9$) it is becoming to ionised forms like H_2AsO_3^- , HAsO_3^{2-} and AsO_3^{3-} (Figure 4). The arsenate, with As oxidation state +5, can be found in an ionised form in a wide pH range ($\text{pH} = 2-14$), as H_2AsO_4^- , HAsO_4^{2-} and AsO_4^{3-} . The factor influencing the As oxidation state is a redox potential, the arsenite compounds occurs in reductive (low redox potential), and the arsenate in a higher redox potential conditions. Moreover the species differs in solubility, i.e. for As(III) oxide and As(V) acid they are 10.1 and 66 g in 100 ml of water, respectively (Andersen et al., 1996).

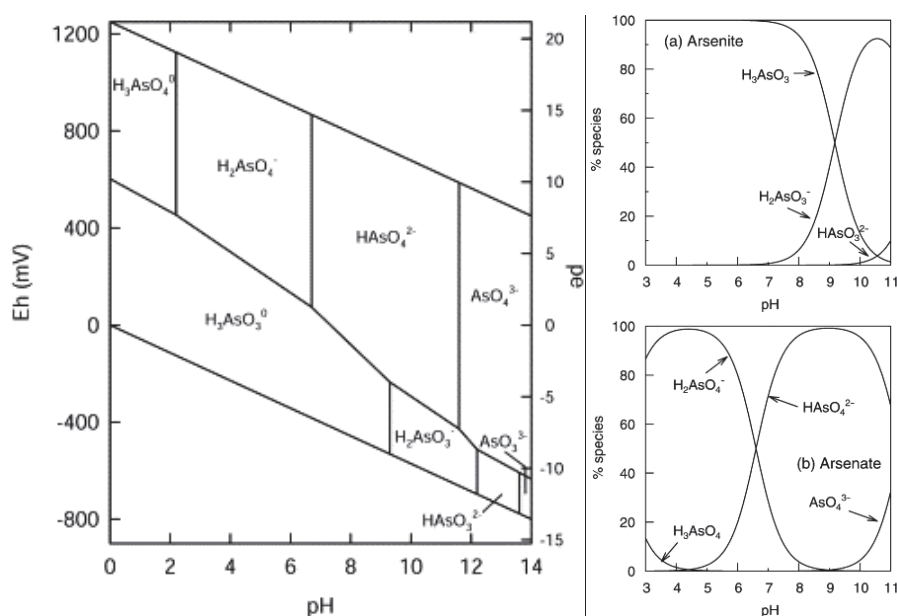
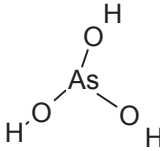
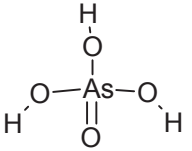
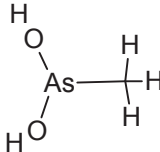
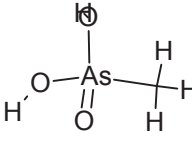
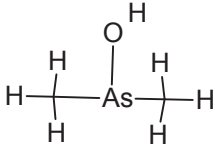
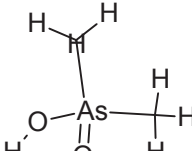
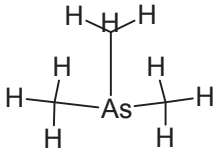
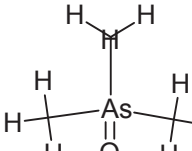


Figure 4 Eh-pH diagram for aqueous As species in the system As–O₂–H₂O at 25 °C and 1 bar total pressure, on the left and (a) Arsenite and (b) arsenate speciation as a function of pH (ionic strength of about 0.01 M; redox conditions have been chosen such that the indicated oxidation state dominates the speciation in both cases) – on the right (reproduced from (Smedley and Kinniburgh, G., 2002) with permission from Elsevier)

An oxidation of arsenite to arsenate can be achieved in presence with help of dissolved oxygen. The As(V) compounds can remain dissolved in solution or be adsorbed on insoluble matter, for example precipitated iron. Arsenate might also form insoluble compounds, like ferric arsenate, or be transformed back into arsenite, if reductive conditions occur. In case of arsenite, it is not only oxidized to arsenate, but also produces arsenic sulphides after reaction with sulphide anion. There are also other arsenic compounds, like organoarsenics, that are a product of methylation occurring with help of bacteria (Lièvremonet et al., 2009). The family of arsenic compounds identified in water are presented in Table 1.

Table 1 Structure of arsenic species identified in water with some pKa values (based on (IARC Monographs 2004))

Name	Structure	Name	Structure
Arsenous acid (arsenite)	 <p>pKa 9.23, 12.13, 13.4</p>	Arsenic acid (arsenate)	 <p>pKa 2.22, 6.98, 11.53</p>
Monomethylarsonous acid - MMA(III)		Monomethylarsonic acid MMA(V)	 <p>pKa 4.1, 8.7</p>
Dimethylarsinous acid DMA(III)		Dimethylarsinic acid DMA(V)	 <p>pKa 6.2</p>
Trimethylarsine TMA		Trimethylarsine oxide TMAO	

2.2. Health effects and occurrence

The arsenic usage as a poison has a long history, unfortunately even a low dose of this element was found to cause adverse health effects, especially for a long period, when it can cause chronic diseases. Generally, it is stated that the As(III) forms are more toxic than the As(V). After an ingestion of the arsenic it can end up in different organs and affect their systems, for example the respiratory, cardiovascular, immune, genitourinary, reproductive, gastrointestinal and nervous systems (Smedley and Kinniburgh, 2001). It was found that arsenic is mostly accumulating in hair and nails, and least in brain tissue (Dang et al., 1983).

A long-term exposure with the lower levels of arsenic which has been also linked to the adverse health effects in a human population. The first reports from the 19th century have connected skin effects (including pigmentation changes, hyperkeratosis and skin cancers) with a consumption of the arsenic in medicines and drinking water (Smedley and Kinniburgh, 2001).

Nowadays the chronic health effects have been described and enclose following diseases:

1) Vascular diseases:

- Peripheral vascular diseases;
- Cardio- and cerebrovascular diseases;
- Hypertension;

2) Cancer:

- Cancers of the lung, bladder and kidney;
- Skin cancer and precancerous lesions of the skin.

Moreover, the arsenic long-term exposure is responsible for neurological adverse effects, like dementia (Dani, 2010). The all health effects caused by the arsenic poisoning are called arsenicosis, which has been also responsible for keratosis, skin changes and hyperkeratosis, skin lesions.

Because arsenic can be dangerous even in small concentrations all over the world are used very rigorous regulations for the maximum concentration of the arsenic in the drinking water. However, allowable concentrations are varying among different countries and corresponds to their development stage, better developed countries have lower arsenic concentration in drinking water (Figure 5).

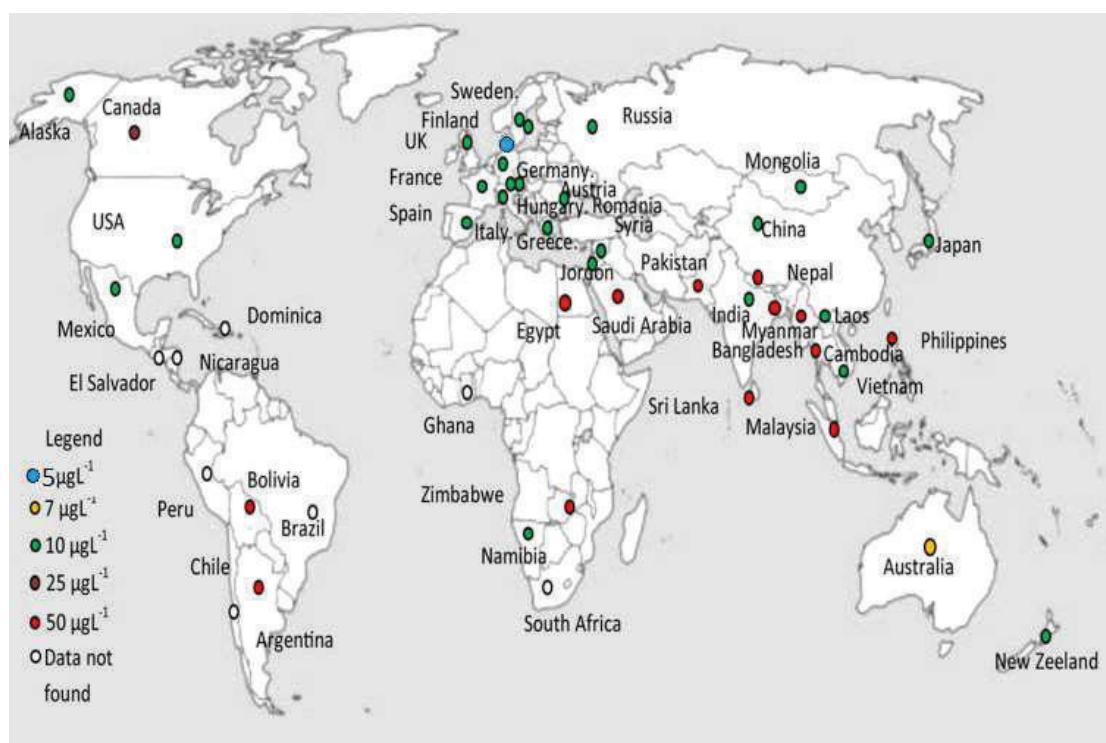


Figure 5 Arsenic affected countries and their respective maximum contamination limits (modified from (Mondal et al., 2013) with permission from Elsevier)

The arsenic compounds in the environment can come from anthropogenic or natural sources. The anthropogenic sources are linked to products, and their production facilities, where arsenic compounds are used, like wood preservatives, paints, dyes, pharmaceuticals, herbicides, and semiconductors (U.S. EPA, 2002). The main anthropogenic sources of the arsenic compounds are mining and smelting industries. Once released, arsenic species can undergo different processes resulting in their distribution in environment. The general pathways of arsenic release are presented on Figure 6. Regardless the arsenic source and distribution pathway in nature the attention shall be made on possibility of involving living organisms (biota), which might have serious repercussions.

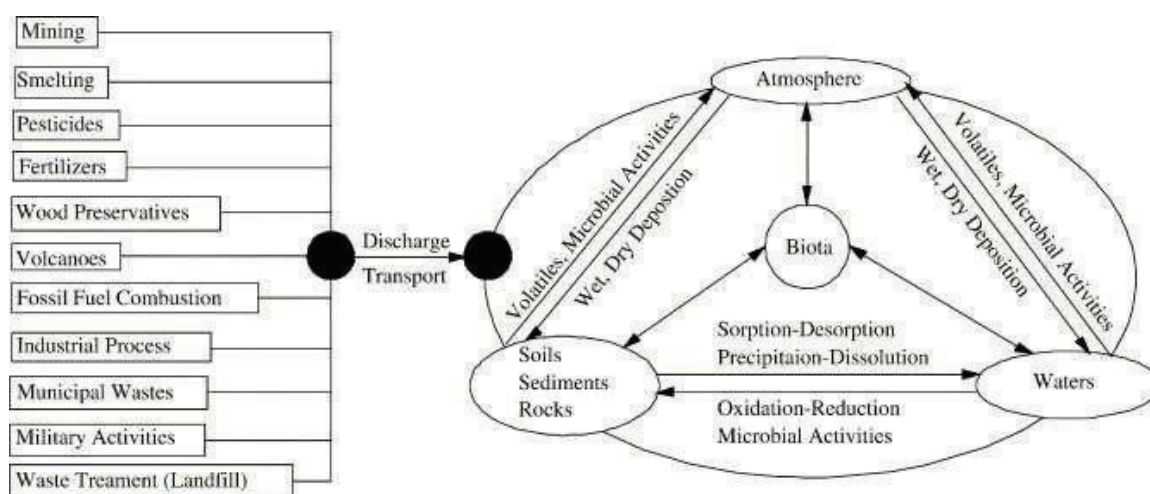


Figure 6 A simplified diagram of arsenic cycle (reproduced from (Wang and Mulligan, 2006) with permission from Elsevier)

Natural arsenic can be found in mineral and hydrothermal veins. The mineral composition depends on the physical and chemical conditions, especially other metals, resulting in diverse minerals compositions and properties (Table 2). Additionally, these minerals can also be found in smaller amounts associated to clays and rocks. Arsenic minerals occurrence in the ground is more problematic as it might influence a groundwater quality. Depending on conditions, like redox and pH, chemistry and microbial activity As can be released from the minerals to groundwater resulting in its elevated content (Islam et al., 2004; Lee et al., 2010; Tadanier et al., 2005). Generally, groundwater with possibility of arsenic contamination appear to be widespread across the world (Amini et al., 2008). However, there is a region, known from high level of arsenic occurrence in groundwater, Bengal Delta in south-east Asia. The worst situation is reported to be in in Bangladesh, where more than 50% of the wells exceed the concentration of the 5 $\mu\text{g/L}$, and in some cases the amount of arsenic exceed 1000 $\mu\text{g/L}$. Therefore, estimated by WHO 57 million of the people that drink arsenic contaminated water ($>10 \mu\text{g/L}$) is called the largest mass poisoning in the history (Steenhuysen, 2010).

Table 2 Some of major arsenic minerals occurring in nature (Smedley and Kinniburgh, G., 2002)

Mineral	Composition	Occurrence
Native arsenic	As	Hydrothermal veins
Niccolite	NiAs	Vein deposits and norites
Realgar	AsS /As ₄ S ₄	Vein deposits, often associated with orpiment, clays and limestones, also deposits from hot springs
Orpiment	As ₂ S ₃	Hydrothermal veins, hot springs, volcanic sublimation product
Cobaltite	CoAsS	High-temperature deposits, metamorphic veins
Arsenopyrite	FeAsS	The most abundant As mineral, dominantly mineral veins
Arsenolite	As ₂ O ₃	Secondary minerals formed by oxidation of arsenopyrite, native arsenic and other As minerals
Claudetite	As ₂ O ₃	Secondary minerals formed by oxidation of realgar, arsenopyrite arsenic and other As minerals
Scorodite	FeAsO ₄ *2H ₂ O	Secondary mineral
Hoernesite	Mg ₃ (AsO ₄) ₂ *8H ₂ O	Secondary mineral, smelter wastes
Conichalcite	CaCu(AsO ₄)(OH)	Secondary mineral
Pharmacosiderite	Fe ₃ (AsO ₄) ₂ (OH) ₅ *5H ₂ O	Oxidation product of arsenopyrite and other As minerals

3. Arsenic removal technologies review

3.1. Current status in arsenic removal technologies

Arsenic can be eliminated from water in a process, where it is physically separated from the solution. The most common technologies for arsenic removal are based on processes of precipitation and coagulation, which involve iron and aluminium salts.

The treatment for arsenic removal is often enhanced by oxidation stage, transforming arsenite to arsenate. The oxidation stage shall be considered on the beginning of a treatment to enable high yield of arsenate, which is easier to remove (Bissen and Frimmel, 2003; Sorlini and Gialdini, 2010). The general comparison of conventional techniques is presented in Table 3. Nevertheless, each technology, having its disadvantages and advantages regarding efficiency and costs, has to be chosen with consideration of the following factors:

- Local guidelines for arsenic level in drinking water;
- Country development stage, in more developed countries can afford more expensive technologies;
- Authority's requirements and restrictions for water treatment technologies.

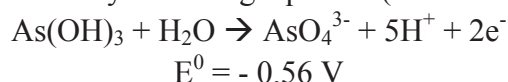
Therefore diverse technologies can be found around the world. Among them adsorption and coagulation-filtration are the foremost ones nowadays. Recent studies tended to favour coagulation-filtration, regarding costs and hazardous waste handling (Jones *et al.* 2013). Integrated approach of different techniques is suggested to be beneficial, and combination of iron based technologies combined with membrane processes are thought to be the most suitable (Mondal et al., 2013). Moreover, the general trend in water treatment is to use as less chemicals and energy as possible, to reduce the costs. Though, selection of the treatment shall be based on water chemistry and process characteristics with regards to the economics.

Table 3 Comparison of some of conventional arsenic removal technologies (Mondal et al., 2013; Parga et al., 2005)

Technology	Advantages	Disadvantages	Removal (%)
<i>Oxidation</i>			
Air oxidation	<ul style="list-style-type: none"> - Relatively simple and low cost process; - Applicable for large water volumes; - oxidizes other inorganic and organic constituents in water; 	<ul style="list-style-type: none"> - Mainly removes arsenic (V) and accelerate the oxidation process - slow process; 	80
Chemical oxidation	<ul style="list-style-type: none"> - Oxidizes other impurities and kills microbes; - relatively simple and rapid process; - Minimum residual mass 	<ul style="list-style-type: none"> - Efficient control of the pH and oxidation step is needed; - Interfering substances decrease efficiency; 	90
<i>Coagulation/flocculation</i>			
Alum coagulation	<ul style="list-style-type: none"> - Simple and cost effective; - Durable powder chemicals are available; - relatively low capital cost and simple in operation; - effective over a wider range of pH 	<ul style="list-style-type: none"> - Produces toxic sludge; - High amount of chemical required; - pre-oxidation may be required; - Additional separation step needed; 	90
Iron coagulation	<ul style="list-style-type: none"> - Common chemicals are available; - More efficient than alum coagulation on weigh basis; - Simple and cost effective 	<ul style="list-style-type: none"> - Medium removal of As(III) ; - Additional separation step needed; 	94.5
<i>Adsorption</i>			
Iron coated sand	<ul style="list-style-type: none"> - Comparatively be cheap and commercially available; - Remove both As(III) and As(V); 	<ul style="list-style-type: none"> - Interferences from competitive anions (PO_4^{3-}; HCO_3^-, SiO_3^{2-}, SO_4^{2-}) - Require regeneration; - Produces toxic solid waste; 	93
<i>Membrane filtration</i>			
Reverse osmosis	<ul style="list-style-type: none"> - High removal efficiency of As(III) and As(V) 	<ul style="list-style-type: none"> - High capital and operational costs (energy required) - High water rejection 	96
Electrodialysis	<ul style="list-style-type: none"> - High removal efficiency; 	<ul style="list-style-type: none"> - Toxic wastewater produced; - High capital and operational costs (energy required); 	95

3.2. Oxidation

The redox oxidation reaction of arsenic compounds, from arsenite to arsenate, in acidic conditions is described by following equation (Sharma et al., 2007):



The arsenite can be oxidized with a help of the common oxidative agents like a hydrogen peroxide, ozone or manganese (IV) oxide and others as in Table 4.

Table 4 Chemical oxidants and their reactions with arsenite (Sharma et al., 2007)

Oxidant	Reaction
<i>Chlorine</i> (Cl ₂)	$\text{H}_3\text{AsO}_3 + \text{HOCl} \rightarrow \text{AsO}_4^{3-} + \text{Cl}^- + 4\text{H}^+$
<i>Chlorine dioxide</i> (ClO ₂)	$\text{H}_3\text{AsO}_3 + 2\text{ClO}_2 + \text{H}_2\text{O} \rightarrow \text{AsO}_4^{3-} + 2\text{ClO}_2^- + 5\text{H}^+$ $5 \text{H}_3\text{AsO}_3 + 2\text{ClO}_2 + \text{H}_2\text{O} \rightarrow 5\text{AsO}_4^{3-} + 2\text{Cl}^- + 17\text{H}^+$
<i>Chloramine</i> (NH ₂ Cl)	$\text{H}_3\text{AsO}_3 + \text{NH}_2\text{Cl} + \text{H}_2\text{O} \rightarrow \text{AsO}_4^{3-} + \text{NH}_4^+ + \text{Cl}^- + 3\text{H}^+$
<i>Hydrogen peroxide</i> (H ₂ O ₂)	$\text{H}_3\text{AsO}_3 + \text{H}_2\text{O}_2 \rightarrow \text{AsO}_4^{3-} + \text{H}_2\text{O} + 3\text{H}^+$
<i>Ozone</i> (O ₃)	$\text{H}_3\text{AsO}_3 + \text{O}_3 \rightarrow \text{AsO}_4^{3-} + \text{O}_2 + 3\text{H}^+$
<i>Permanganate</i> (MnO ₄ ⁻)	$3\text{H}_3\text{AsO}_3 + 2\text{MnO}_4^- \rightarrow 3\text{AsO}_4^{3-} + 2\text{MnO}_2 + 7\text{H}^+ + \text{H}_2\text{O}$
<i>Ferrate</i> (FeO ₄ ²⁻)	$3\text{H}_3\text{AsO}_3 + 2 \text{FeO}_4^{2-} + \text{H}_2\text{O} \rightarrow 3\text{AsO}_4^{3-} + 2\text{Fe(OH)}_3 + 5\text{H}^+$

The most common and easiest to use oxidative agent is molecular oxygen that can be delivered to the solution in contact with atmospheric air. Though oxygen is not as efficient as the other chemical oxidants, a half-life of As(III) oxidation by help of oxygen is a couple magnitudes higher than for the previously presented chemical oxidants in Table 4 for which it was in range of milliseconds to hours (Sharma et al., 2007). However, low costs and easy access made aeration process applicable in full scale arsenic treatments (Kowalski et al., 2013; Zikoudi et al., 2008; Jessen et al., 2005). Furthermore, the half-time of oxidation can be noticeably reduced in the presence of iron and manganese ions, as it is indicated in Table 5.

Table 5 Half-lives of the oxidation reactions of As(III) in groundwater (Kim and Nriagu, 2000)

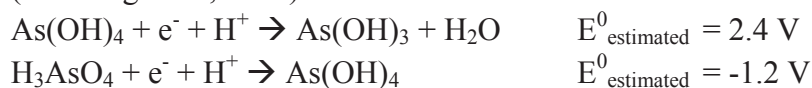
Groundwater	Oxidant	T _c (half-live)
Higher Fe and Mn concentration	Ozone	4.2 min
	Oxygen	2.2 days
	Air	4.0 days
Lower Fe and Mn concentration	Ozone	4.5 min
	Oxygen	4.8 days
	Air	8.9 days

The simplest explanation of manganese and iron role, in form of Mn(IV) and Fe(III), is that they can be a primary electron acceptors in the oxidation of As(III), which is thermodynamic feasible. However, the kinetics of redox reaction, especially between Fe(III)oxide and As(III), were found to be relatively slow (Oscarson et al., 1981). Another study proposed mechanisms in which pseudo-Fenton reagent is produced in oxygen-rich water and in the presence of iron (II) ions. The mechanism of iron (II) and dissolved oxygens role in As(III) oxidation is shown in Table 6. The attention shall be given to the presence of As(IV) and Fe(VI), which are intermediate species in the proposed reactions pathways. The existence of the intermediates was studied in a number of kinetic models of arsenic oxidation with help of Fenton reaction (Klaening et al., 1989; Lenoble et al., 2002; Hug and Leupin, 2003; Sharma et al., 2007; Li et al. 2012; Wang et al., 2013)

Table 6 Reactions proposed for Fe(II) enhanced oxidation of As(III) in air (Sahai et al., 2007)

Reaction
Fe (II) oxidation generating reactive oxygen species
$\text{Fe(II)} + \text{O}_2 \rightarrow \text{Fe(III)} + \text{O}_2^{*-}$
$2\text{Fe(II)} + 2 \text{O}_2^{*-} + 4\text{H}^+ \rightarrow 2\text{H}_2\text{O}_2 + 2\text{Fe(III)}$
$\text{Fe(II)} + {}^*\text{OH} \rightarrow \text{Fe(III)} + \text{OH}^-$
$\text{Fe(II)} + \text{H}_2\text{O}_2 = \text{Fe(III)} + {}^*\text{OH} + \text{OH}^-$ (Fenton reaction)
$\text{Fe(II)} + \text{H}_2\text{O}_2 \rightarrow 2 \text{OH}^- + \text{Fe(IV)}$ (Additional intermediate oxidant generation)
As (III) oxidation
$\text{Fe(IV)} + \text{As(III)} \rightarrow \text{Fe(III)} + \text{As(IV)}$
$\text{As(IV)} + \text{O}_2 \rightarrow \text{As(V)} + \text{O}_2^-$
Net redox reactions
$4 \text{Fe(II)} + \text{O}_2 + 10 \text{H}_2\text{O} = 4 \text{Fe(III)(OH)}_3 + 8\text{H}^+$
$2 \text{H}_3\text{As(III)O}_3 + \text{O}_2 = 2\text{H}_2\text{As(V)O}_4^- + 2\text{H}^+$

Fe(IV) was used in diverse studies to represent the oxidant, Fenton intermediate, produced in the Fe(II)/O₂ system at near-neutral pH (Bataineh et al., 2012; Hug and Leupin, 2003; Li et al., 2012). As(IV) represents various species that reacts directly with molecular oxygen or radicals in very fast reactions. As(IV) species are both very strong oxidants and reductants, with following estimated standard potentials (Klaening et al., 1989):



The intermediates were applied in the advance kinetic model that provides estimates for reaction rate constants. The studies of Hug and Leupin 2003 brought significant data about redox reactions in the environment and in arsenic removal processes. It was observed that As(III) was oxidized in parallel to the oxidation of Fe(II) by O₂ and by H₂O₂ and, foremost, oxidation is not inhibited by ^{*}OH radical scavengers at neutral pH (Hug and Leupin, 2003).

3.3. Coprecipitation and adsorption of arsenic

The precipitation process is based on an occurrence of non-soluble arsenic compounds. Although the process reduces arsenic compounds solubility, it does not guaranty an elimination of arsenic to desirable limit. For example it was possible to gain an arsenic solubility reduction from 6430mg/l to 0.823 mg/l in a process of the arsenic sludge waste neutralization that used high excess of calcium and ferric additives (Palfy et al., 1999).

The main focus of the arsenic removal has been directed to the coprecipitation, where elements (both dissolved and particulate) are adsorbed onto and trapped within the precipitate, which is then settled out to leave a purified effluent. (Merrill et al., 1986). Concerning the arsenic compounds adsorption some hydroxides, of aluminium and iron, have been found to be useful and their usage have been widely described.

The most broadly used, and hence described, are processes based on iron compounds. The main advantage of iron compounds are their properties in circum-neutral pH, where they occur as non-dissolved particles of the different iron oxides and hydroxides. In the same conditions arsenic (V) compounds, H_2AsO_4^- and HAsO_4^{2-} , appear enabling their coprecipitation on solid phase of iron (III) hydroxides, as shown on Figure 6. The main process which involves iron hydroxides in the arsenic removal is coagulation. However mechanisms of physicochemical reactions between the hydroxides and arsenic compounds are not clear in detail, but four theories are recently taken into consideration:

1. Precipitation, the formation of the insoluble compounds such as FeAsO_4 ;
2. Coprecipitation, the incorporation of soluble arsenic species into the growing iron hydroxide phase;
3. Occlusion, the entrapment of adsorbed arsenic species in the interior of the growing iron hydroxide phase;
4. Adsorption, the binding of soluble arsenic to the external surfaces of the insoluble iron hydroxide (Phenrat et al., 2008).

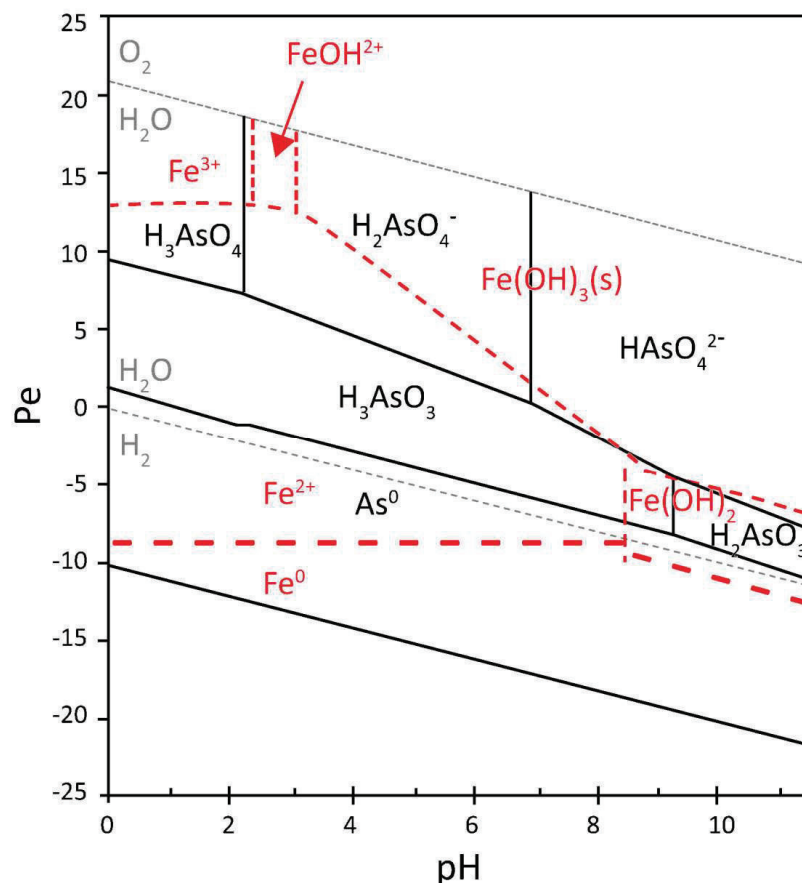


Figure 7 Pe–pH diagram for the As–Fe–H₂O system at 25 °C. Total As = 4 μM; total Fe = 10⁻⁴ M (reproduced from (Bang *et al.* 2005) with permission from Elsevier)

The arsenic compounds sorption is not limited to pH and redox potential, that controls arsenic speciation, but also depends on form of iron oxides. Even though these iron oxides might have a similar chemical composition they differ in structure. Initially formed amorphous iron hydroxide distinguish with high specific surface area, but, over time, undergo transformation to more crystalline forms, such as goethite or hematite (Dixit and Hering, 2003). The differences in surface complexation kinetics of the arsenite and arsenate sorption on the surface among iron minerals, are presented in Table 7. The binding strengths of As(III) and As(V) for the various iron oxides are comparable, although general performance of iron coagulation is said to be in favor of As(V), which shall be considered in the treatment design (Mohan and Pittman, 2007). However, for amorphous iron oxide and goethite, As(V) sorption was found to be more favorable than As(III) at lower pH values, but the opposite situation occur at higher pH values (above 6.5)(Dixit and Hering, 2003).

Table 7 Intrinsic Surface Complexation Constants for Sorption onto Iron Oxide Minerals

Adsorption reaction	Amorphous iron oxide ¹	Goethite ¹	Magnetite ¹	Iron hydroxide ²
$\equiv\text{FeOH} + \text{H}^+ \rightarrow \equiv\text{FeOH}_2^+$	7.29	7.47	4.60	
$\equiv\text{FeOH} \rightarrow \equiv\text{FeO}^- + \text{H}^+$	-8.93	-9.51	-8.20	
Arsenate adsorption constant				
$\equiv\text{Fe-OH} + \text{AsO}_4^{3-} + 3\text{H}^+ \rightarrow \equiv\text{Fe-H}_2\text{AsO}_4 + \text{H}_2\text{O}$	29.88	31.00		29.31
$\equiv\text{Fe-OH} + \text{AsO}_4^{3-} + 2\text{H}^+ \rightarrow \equiv\text{Fe-HAsO}_4^- + \text{H}_2\text{O}$	24.43	26.81		23.51
$\equiv\text{Fe-OH} + \text{AsO}_4^{3-} + \text{H}^+ \rightarrow \equiv\text{Fe-AsO}_4^{3-} + \text{H}_2\text{O}$	18.10	20.22		10.58
Arsenite adsorption constants				
$\equiv\text{Fe-OH} + \text{AsO}_3^{3-} + 3\text{H}^+ \rightarrow \equiv\text{Fe-H}_2\text{AsO}_3 + \text{H}_2\text{O}$	38.76	39.93	38.41	40.20
$\equiv\text{Fe-OH} + \text{AsO}_3^{3-} + 2\text{H}^+ \rightarrow \equiv\text{Fe-HAsO}_3^- + \text{H}_2\text{O}$	31.87	32.40	33.02	

1(Dixit and Hering, 2003), 2 (Kim and Nriagu, 2000)

Regarding the application of the coprecipitation process it was found that freshly precipitated Fe(III) (hydr)oxides, as a result of Fe(II) oxidation, hydrolysis and precipitation, have a higher sorption capability than directly dosed Fe (III) compounds (Roberts and Hug, 2004). Moreover, the presence of Fe(II) ions was found to increase the oxidation rate of As(III) in an oxygen rich environment, as it was discussed in the previous section. However, some limitations, linked with the presence of oxyacids (like H_4SiO_4 , HCO_3^- , $\text{H}_2\text{PO}_4^{2-}$ and HPO_4^-), shall be considered when applying iron based techniques. It was found that these oxyacids behave similarly to arsenic compounds and compete for adsorption sites on the iron oxide minerals, resulting in lowering the removal efficiency. For example hydroxylapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$, HAP) was found to be a main naturally occurring sources of competing ion in Bangladesh groundwater. Beside the competition with As compounds the oxyacid ions may inhibit precipitation of the ferric oxyhydroxide phase resulting in reduction of coprecipitated arsenic. Although it was found that the oxyacids greatly affected the amount of arsenic uptake in the As(III) systems, only a minimal effect on arsenic uptake in the presence of the HAP was found. Among the oxyacids silicate and phosphate were found to reduce arsenic removal and have the worst effect, which was 67% and 63%, respectively, which are less by 5% and 9% than the systems without competing oxyacids. The arsenic uptake was even more reduced, to 52%, when all oxyacids were present (Ciardelli et al., 2008). Other studies of combined effect of different anions on apparent adsorption constants indicated that the affinity of the anions for iron hydroxides sites decreased in the following order arsenate>phosphate>arsenite>silicate>bicarbonate (Meng et al., 2002). For that reason the most significant is a presence of phosphates that have the same affinity to iron hydroxides as arsenic compounds, and are reported to be responsible for significant

reduction of As sorption on iron precipitates (Meng et al., 2002; Sahai et al., 2007). A consequence of phosphate presence is a consideration of the Fe/P ratio for prediction of arsenic removal efficiency. The study of application of biosand filters in Cambodia revealed that an increase of the Fe/P ratio, due to either an increase of Fe or a decrease of phosphate concentrations, will improve arsenic removal effectiveness dramatically (Figure 6). The presence of moderate Fe (>0.1 mg/L) and P (>0.5 mg/L) concentrations in the studied waters explains the variable and often inefficient removal of arsenic by sand filters (Chiew et al., 2009).

Beside the inorganic compounds, the role of natural organic matter (NOM), in form of humic substances, was also studied. It was found that arsenic removal was limited by the presence of humic acids because of the formation of soluble Fe-humate in groundwater which hindered the production of iron precipitates (Rao et al., 2009)

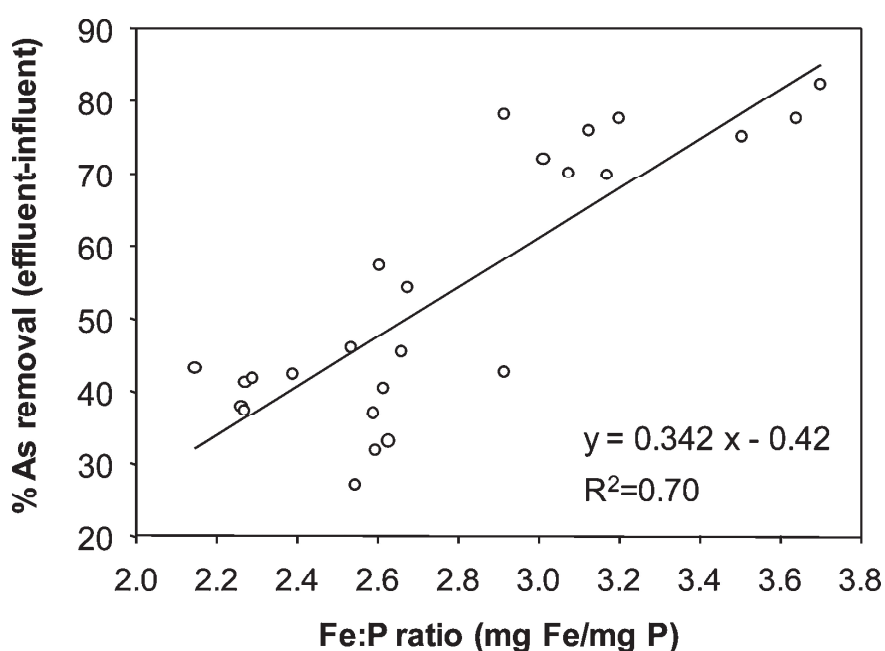


Figure 8 Relationship between ratio of Fe/P on arsenic removal efficiency. If the inlet iron content concentration is high or increases and/or inlet phosphorus concentration is low or reduces, arsenic removal efficiency increases dramatically (Reprinted with permission from (Chiew et al., 2009) Copyright 2009 American Chemical Society)

3.4. Strategies for iron supplementation

To apply iron coprecipitation of arsenic in water treatment different approaches for iron compounds supplementations have been introduced:

- Iron salt solution dosage;
- Zero-valent iron;
- Iron electrolytic dissolution (electrodissolution).

From the practical point of view it is important to the most efficient method, regarding costs, energy and eventual additives, like pH adjustment.

3.4.1. Iron salts dosage

Coagulation, enhanced with filtration, with iron salts is a well-established, efficient method for large scale water treatment, in either the absence or the presence of As. (Bundschuh et al., 2010). Different iron salts can be used as a source of ferric or ferrous ions. A statistical experiment design method was used to investigate the effects of initial arsenate concentration, type of coagulant, its dose and pH on the arsenic removal performance. According to results shown in Table 8, Fe(III)-bearing salts were found to be more suitable than FeSO₄, regarding dose and optimum pH, that does not require corrections to the pH range 6-8 required for drinking water. Among the Fe(III) salts the more efficient was use of ferric sulfate, as it required lower dose of Fe(III) ions (comparing molar concentration and the fact that 1 M of Fe₂(SO₄)₃ produces 2 M of Fe³⁺). Optimum pH values for maximum arsenate removal for ferric chloride, ferric sulfate and ferrous sulfate were found as 7.5, 8 and 9, respectively (Baskan and Pala, 2009).

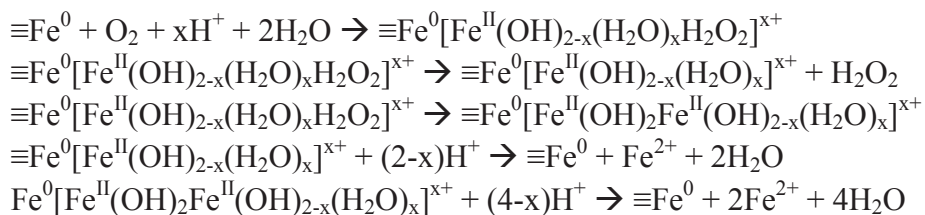
Table 8 Obtained highest arsenate removal efficiencies (Eff.) in the optimum pH (Opt. pH) and the optimum coagulant dose (adapted from (Baskan & Pala 2009))

Coagulant type	Opt. pH	Initial As(V) concentrations					
		10 µg/L		500 µg/L		1000 µg/L	
		Dose (ppm/mM)	Eff. (%)	Dose (ppm/mM)	Eff. (%)	Dose (ppm/mM)	Eff. (%)
FeCl ₃	7,5	50/0.31	88	31/0.19	100	37/0.23	100
Fe ₂ (SO ₄) ₃	8	40/0.1	70	28/0.07	100	32/0.08	100
FeSO ₄	9	60/0.39	63	60/0.39	91	58/0.38	100

3.4.2. Zero valent iron

The primary advantages of zero-valent iron (ZVI), elemental iron in every form that has elevated area to contact with the aqueous solution, include low cost, simplicity in handling and scalability, and the formation of strong adsorption complexes between iron oxide reaction products and dissolved As(III) and As(V) (Manning et al., 2002). Its implementation was reported to help to treat different inorganic contaminants, like Cr(VI), As, Mn, Mo, Se, U, V and Zn (Melitas et al., 2001; Morrison et al., 2002). Application of the ZVI is based on a spontaneous corrosion process that takes place, when water contacts with iron surface enabling redox reactions to go on as shown in Table 9. To produce iron hydroxides, after formation of iron ions and their further oxidation, an electron acceptor is required, and the simplest available is molecular oxygen. However, production of iron compounds is to be limited by the oxygen availability. The studies revealed that nanoscale zero-valent iron is capable of enacting distinctive reactive pathways to create higher iron oxidation states without oxygen involvement. This phenomena was found to be possible not only by H₂O reduction and molecular hydrogen evolution production, but also by reduction of metal cations, like Hg²⁺ (Reardon, 1995; Yan et al., 2010).

Nevertheless, the corrosion of the ZVI in oxygen rich environment has revealed some mechanisms resulting in production of oxidative species by the following reactions on the iron surface:



Produced hydrogen peroxide can react with the main corrosion products – iron (II) ions and in effect produce hydroxide radicals, as it was shown in Table 6. A proposal of the mechanism initiated a discussion whether the arsenite is oxidized mainly in a solution by the Fenton reagent, rather than to be removed by sorption on freshly formed hydrous ferric oxide (Katsoyiannis et al., 2008). However the creation of hydrogen peroxide on the Fe^0 surface has been discussed to be uncommon at these conditions. The new interpretation pointed out an adsorption/surface-oxidation mechanism that combines firstly the adsorption or coprecipitation followed by the arsenite oxidation on the iron surface (Katsoyiannis et al., 2009; Noubactep, 2009; Pang et al., 2011).

Table 9 Relevant reactions for the process of aqueous Fe(0) dissolution and oxide scale formation in a passive remediation Fe(0)/H₂O system (Noubactep and Schöner, 2010)

Process	Reaction	
Fe(0) dissolution	$\text{Fe}(0) \leftrightarrow \text{Fe}^{2+} + \text{e}^-$	(1)
Fe(0) passivation	$\text{Fe}(0) + \text{H}_2\text{O} \rightarrow \text{Fe}(\text{O})_{\text{ads}} + 2\text{H}^+ + 2\text{e}^-$	(2)
Fe(0) depassivation	$\text{Fe}(0)_{\text{ads}} + 2\text{H}^+ \rightarrow \text{Fe}^{2+} + \text{H}_2\text{O}$	(3)
	$\text{Fe}(0)_{\text{ads}} + \text{H}_2\text{O} \rightarrow \text{Fe}(\text{OH})_2$	(4)
	$\text{Fe}(0)_{\text{ads}} + \text{OH}^- \rightarrow \text{HFeO}_2^-$	(5)
H ₂ evolution	$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\uparrow$	(6)
O ₂ reduction	$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$	(7)
Fe ²⁺ oxidation	$\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^-$	(8)
	$\text{Fe}^{2+} + 2\text{OH}^- \rightarrow \text{Fe}(\text{OH})_2$	(9)
	$\text{Fe}^{3+} + 3\text{OH}^- \rightarrow \text{Fe}(\text{OH})_3$	(10)
Scale formation	$\text{Fe}(\text{OH})_2 \rightarrow \text{FeO} + \text{H}_2\text{O}$	(11)
	$2\text{Fe}(\text{OH})_3 \rightarrow \text{Fe}_2\text{O}_3 + 3\text{H}_2\text{O}$	(12)
	$4\text{Fe}(\text{OH})_3 \rightarrow \text{Fe}(\text{OH})_2 + \text{Fe}_3\text{O}_4 + 5\text{H}_2\text{O} + \frac{1}{2}\text{O}_2$	(13)
	$\text{Fe}(\text{OH})_3 \rightarrow \text{FeOOH} + \text{H}_2\text{O}$	(14)

3.4.3. Iron electrodisolution

An electrolytic iron generation is a process where direct current voltage is applied to electrodes releasing iron ions from metallic iron anode, and water acts as electrolyte. The generation of iron ions in electrochemical process was found useful for coagulation, where formation of iron hydroxides enables flocculation and coagulation of suspended solids. The process is called electrocoagulation (EC), and has been known for decades (Moreno C. et al., 2009). The process of electrocoagulation can be divided into two main stages:

- 1) Iron electrodisolution - formation of ions take place at the anode, their hydrolysis and parallel electrolysis of water, which correspond to reactions 1 and 6-10 from Table 9
- 2) Formation of flocs and reactions with contaminants, which depends on the conditions.

The reactions occurring at the anode and in a bulk solution are present on Figure 9.

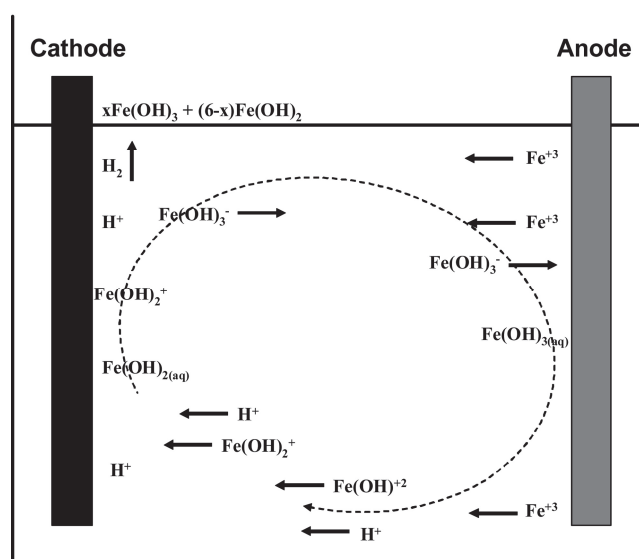


Figure 9 Migration of cations and anions in the electro-coagulation reactor (Reprinted with permission from (Moreno C. et al., 2009) Copyright 2009 American Chemical Society)

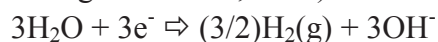
The electrolytic process shall follow Faradays law, according to which the mass of iron released from the anode can be calculated from the following equation:

$$m_{\text{Fe}} = \frac{I \times t}{F} \times \frac{M}{Z}$$

m_{Fe} – mass of released iron [g] ; I – current of energy source applied [A], t – time [s]; F – Faraday constant [96485 C/mol]; M – molar mass of iron [56 g/mol]; z - is the valence number of ions of the substance – in case of Fe^{2+} release it is 2.

Therefore the process can be easily manipulated by applying specific current. However, it can be also limited by different factors linked with the process and the treated water quality. For example, it was found that dissolution and passivation rate of iron strongly depends on the electrode potential, the composition of the electrolyte, and the pH (Lorenz et al., 2002).

Regarding water quality bicarbonates were found to precipitate as carbonates at the cathode as a consequence of a reduction reaction that raises the interfacial pH by following reactions (Peraza Barrios et al., 2007; Yanagisawa and Matsumura, 2011; Yanagisawa et al., 2008):



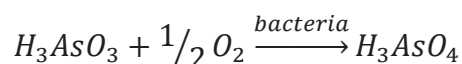
Nevertheless, the iron electrodisolution was proved as a cheap Fe(II) dosage method and able to efficiently remove arsenic in various application (Koby et al., 2011; Lacasa et al., 2011; Majumder and Gupta, 2011).

3.5. Use of biotechnology for arsenic removal

There are microorganisms, which are not only resistant to arsenic toxicity but are able to make use of it. There are biochemical processes, like arsenite oxidase, respiratory arsenate reductase or cytoplasmic arsenate reductase, where arsenic is being incorporated into microorganisms (Silver and Phung, 2005). In a consequence of these processes some bacteria species were found to help in arsenic removal by being involved in oxidation and sorption processes.

3.5.1. Microbiological oxidation

Desirable reaction of As(III) transformation to As(V) can be achieved by help of bacterium species. Some organisms use the As(III) oxidation for detoxification purposes, catalyzing arsenite oxidation with oxygen (Katsoyiannis and Zouboulis, 2004):



The variety of bacteria species performing the above reaction are known as arsenite oxidizers and were reported in different studies. Most of them were found in environment where naturally arsenic compounds occur, soil and mines, enabling to evolve bacteria organisms that can survive in such location, Table 10. The arsenite oxidizers were investigated regarding their tolerance to arsenic and arsenite oxidation rate, which are presented in the table. Although there is a number of As-oxidizing bacteria species in environment, only few of them can be used for drinking water treatment purposes. First of all microorganisms applied for water processing cannot be pathogenic or influence a human health in any way. Moreover, the species shall also have very low nutrition requirement, and preferable would be those which use As(III) as a energy source. An example of species fulfilling the requirements is a CASO1 population, selected from a mining site. The main features of the population, which make them beneficial for water treatment processes are following:

- (i) it is autotrophic and needs only a low nutrient supply;
- (ii) it preserves its ability to oxidize As(III) over a large interval of pH, temperature and As(III) concentration;
- (iii) high As(III)-oxidizing rates were obtained in a fixed-bed reactor (Battaglia-Brunet et al., 2002).

Another promising species are iron oxidizing bacteria, like *Gallionella ferruginea* and *Leptothrix ochracea*. These bacteria were found to effectively oxidize As(III) during biotic oxidation of iron, that is a basis of simple and efficient method for iron and arsenic removal with help of sand media filtration. Moreover, deposited iron oxides in a filter medium together with microorganisms offers favourable conditions for arsenic adsorption (Katsoyiannis et al., 2002; Sogaard et al., 2001). However more detailed investigations of Fe-rich biofilm developed during the biological Fe removal indicates that other genus, than *Leptothrix* and *Gallionella*, was found to promote As(III) (Casiot et al., 2006). Therefore current investigations focus on identification of bacteria strains found in arsenic treatment systems, mechanisms involving arsenic compounds and their applicability to water treatment.

Table 10 Summary of studies of arsenite oxidizers (Salmassi et al., 2002)

Microorganism	Isolation Environment	Ambient As	Experimental As [mM]	V _{max} - kinetic constant
<i>Pseudomonas arsenoxydans</i>	Cattle-dipping fluids	NR	20-100	100 µM/mg N/h
<i>Xanthomonas arsenoxydans</i>				31 µM/mg dry wt./h
Soil consortium	Soil	NR	2.5–40	NR
<i>Alcaligenes faecalis</i>	Raw sewage	NR	10–20	0.05 µmol/mg protein/min
<i>Alcaligenes</i> strain	Soil	NR	0.24–2.4	6.7 µl O ₂ /min (ca. 10 ¹⁰ cells)
Seawater consortium	Coastal water	<70 nM	0.0013	3.-9.2 µM/hr
<i>Alcaligenes faecalis</i> Purified enzyme	-*	NA	0.20	0.023 µmole/mg protein/min
<i>Agrobacterium albertimagni</i>	Macrophyte surfaces	2.7 µM	0.002-5	(1.81±0.58)×10 ⁻¹² µmole/cell/min
Strain AOL15				0.043±0.017 µmole/mg protein/min

*-previously isolated bacterium; NR – not reported; NA – not applicable

3.5.2. Biologically enhanced sorption

Microorganisms can also play an important part in the sorption process of arsenic compounds. Their role can be twofold, by direct sorption on microorganisms or sorption on compounds produced by them, i.e. bioproducts.

Direct sorption of arsenic was found to take place on the different microorganisms and media's, like anaerobic or fungal biomass (Chowdhury and Mulligan, 2011; Pokhrel and Viraraghavan, 2008). For example Fe(III)-treated *Staphylococcus xylosus*, was found also to be useful for treatment of Cr(VI) and As(V) mixture. However, the process was found to be spontaneous and driven by randomness sorption of the species at the solid/solution interface, which might result in difficulties of optimizing the process for the full scale treatment (Aryal et al., 2011). More interesting is an example of iron based bioproducts formed by microorganisms. A biogenic schwertmannite, a form of the iron precipitate – $\text{Fe}_8\text{O}_8(\text{OH})_{4.42}(\text{SO}_4)_{1.79}$, was produced by *Acidithiobacillus ferrooxidans* and was found to play an important role in adsorption of As(III) from water. The process could have occurred thanks to formation of schwertmannite particles as a result of ferrous sulfate oxidation by the bacteria cells making a possible effective arsenic removal from groundwater with a high adsorption capacity of As(III) in pH range of 7–10. An As(III) incorporation into the schwertmannite structure involving of ligand exchanges between As(III) species and surface hydroxyl group and sulphate was indicated as an occurring mechanism, but more insight are needed before applying the method for water production (Liao et al., 2011).

4. Application of novel techniques for As removal

MicroDrop Aqua (MDA) system was invented for removing arsenic trace level without external addition of chemicals but is based on the novel iron addition methodology followed by the specially designed aeration unit, as presented in Figure 10. The process is based on iron dosage by help of zero-valent iron (ZVI) or electrolytic iron dissolution (Fe-ED). The dosage delivery is followed by an aeration device where the stream of water is broken into smaller parts by help of layers of polymer grid pipes, resulting in increasing of contact interface between water and air. As a result of the iron dosage before the aeration precipitation and deposition of iron hydroxides on the polymer material occurs.

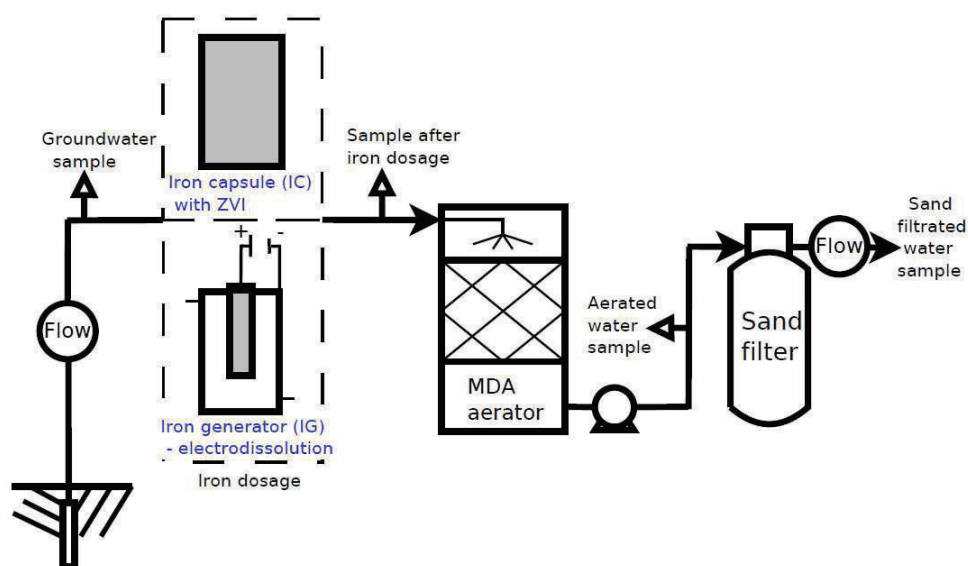


Figure 10 Scheme of MDA arsenic removal treatment; iron capsule with ZVI or iron generator with Fe-ED used for iron dosage are followed by the MDA aeration unit and sand filter.

4.1. System performance

The performance of two different sites, where the MDA systems were implemented is presented on Figure 11. The systems differed in the iron dosage methods, i.e. one had the iron capsule (IC) with the ZVI and other the iron generator. Both systems were equipped with the MDA aeration unit and sand media filter. The treatments did not differ in the general mechanism of the arsenic removal. First, groundwater was firstly supplemented with ferrous ions at the anoxic conditions in the IC or the IG, from where it was mixed with air in the aeration unit, saturating water with dissolved oxygen, resulting in a partly oxidation of ferrous ion and arsenite. The inorganic species, iron and arsenic, are removed by coprecipitation in sand filter. By letting the system run for a longer period it was possible to obtain an iron dose necessary for efficient arsenic coprecipitation in the sand filtration unit. The dose, as a Fe/As ratio, could be obtained from backwash sludge that is produced on regularly basis during the sand filter maintenance. As it can be noticed in Table 11 the systems differed in the Fe/As ratio found in the backwash sludge. The differences in ratios indicate that

iron electrodisolution might have required lower iron dosage. However the sand filter performance and the especially role of other ions cannot be neglected.

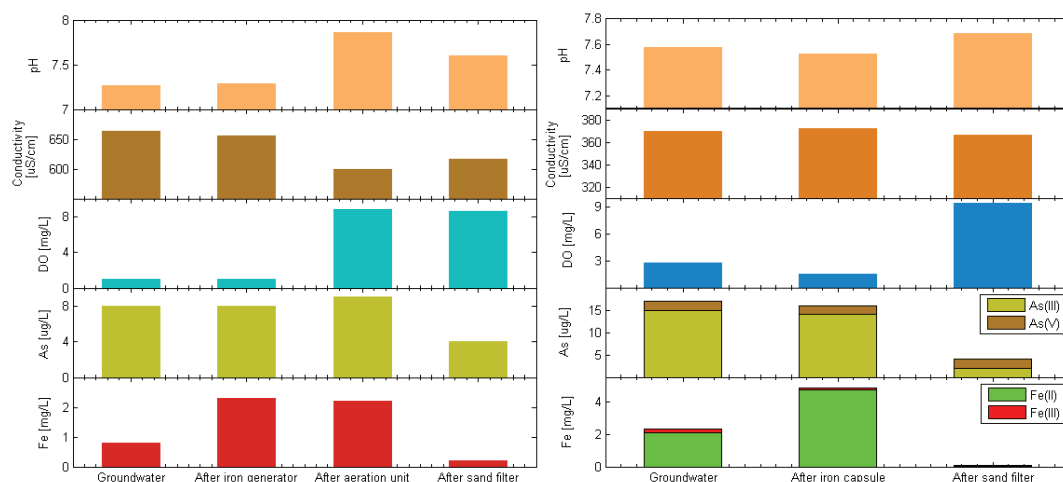


Figure 11 Water parameters at each stage of treatment with use of Fe-ED (IG current of 2.1A and flow 0.28 L/s) - on the left and ZVI- on the right; from top: pH; conductivity; dissolved oxygen; As concentration; Fe concentration

Table 11 Comparison of the sand filter backwash sludge samples collected from different water works

Iron dosage method	As [mg/g]	Fe [mg/g]	Mn [mg/g]	Mg [mg/g]	Ca [mg/g]	Fe/As ratio [mg/mg]
Iron generator	3.3	225	0.29	3.0	65	68
Iron capsule	1.4	226	6.6	0.5	22	166

4.2. Iron addition

Devices used for the iron supplementation in the waterworks are shown on Figure 12. The main difference between the implementation of the ZVI and Fe-ED is the control of produced ions. The ZVI, when solely used, is driven by spontaneous redox reactions, where no control of formed Fe^{2+} takes place. Moreover the ZVI has irregular distribution of anodic (iron releasing) and cathodic (electron acceptor) sites that take part in the iron release. Therefore, the implementation of the ZVI might not give the desirable effect at once and a long period of process optimization might be required to find the proper amount of ZVI source and residence time in the iron capsule for achieving specific iron dosage, as it is shown on Figure 13.



Figure 12 Danish waterworks, where the system is mounted with the ZVI capsule (pictures on the left) and the Fe-ED (on the right); the iron generator is connected to the aeration unit on the right lower picture (courtesy of MicroDrop Aqua ApS, Denmark)

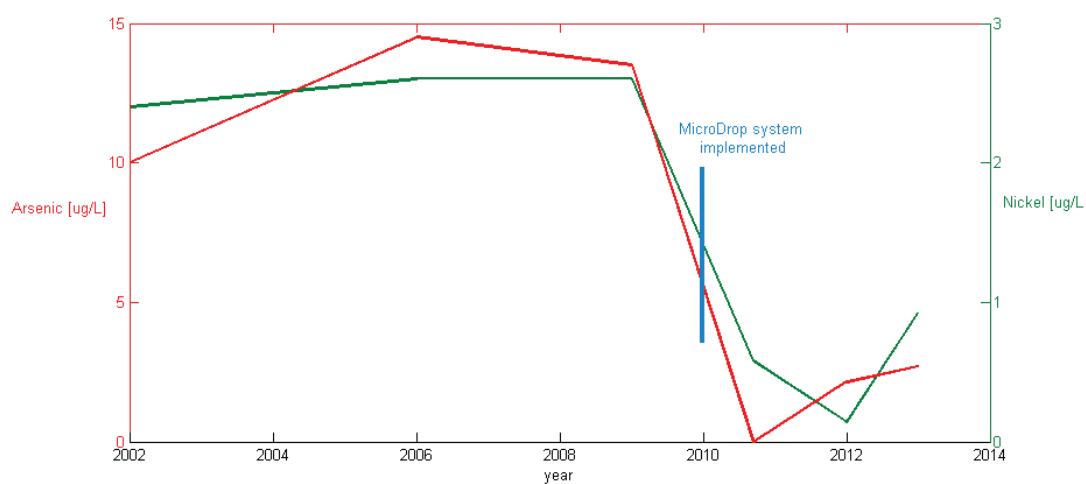


Figure 13 Arsenic and nickel removal efficiency before and after the MicroDrop system with the ZVI, as presented on Figure 10, was implemented at the Danish waterworks (groundwater contains about 18 $\mu\text{g/L}$ As)

More promising is the usage of the Fe-ED that is driven by an applied voltage to an iron sacrifice anode. It is enabling the control of the amount of electrons taking part in the process. The process follows the Faraday law and the iron dose can be calculated from the measured current. The Fe dose (N), as a mass of iron released from anode during time (t), can be found by help of the following equation:

$$N = \frac{m_{Fe}}{t} = C_{Fe,produced} \times Q = \frac{I \times M}{F \times z}$$

Where Q – water flow rate [L/s], $C_{Fe,produced}$ - concentration of produced Fe [mg/L]; m_{Fe} – mass of released iron [g] ; I – current of energy source applied [A], t – time [s]; F – Faraday constant [96485 C/mol]; M – molar mass of iron [56 g/mol]; z - is the valence number of ions of the substance - in case of Fe^{2+} release it is 2.

With use of the above equation it is possible to optimize the arsenic removal, as there is a clear correlation between the applied current to the iron anode and the quality of produced water (Figure 14).

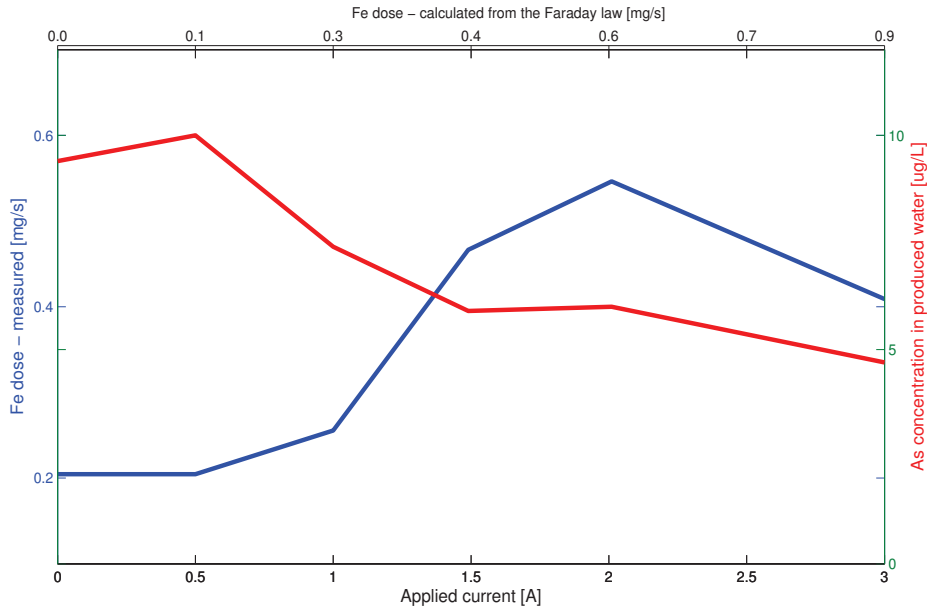


Figure 14 Correlation between the applied current (theoretical Fe dose) and produced water quality in waterworks where the Fe-ED process was used as presented on Figure 10

However, a long usage of the iron generator revealed occurrence of carbonate scaling depositing on the cathode surface, beside iron oxyhydroxides, like hematite, schwertmannite and goethite, found on the anode surface. The scale surface is building up, as a consequence of calcium and magnesium bicarbonates presence in treated water having been found to be responsible for an decreasing efficiency of the iron release process. The mechanisms responsible for scaling are based on the reduction reaction at the cathode, where electrons are taken up by water that result in increase of amounts of OH^- and therefore the interfacial pH sufficiently to precipitate the carbonates.

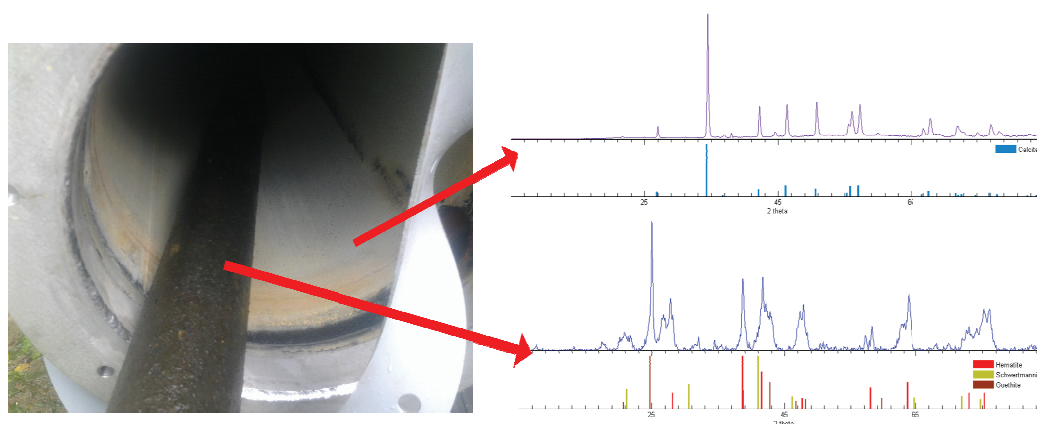


Figure 15 XRD analysis of cathode (stainless steel wall) and iron rod anode residuals after long implementaion the Fe-ED process

The presence of scale forming compounds has to be considered not only in the Fe-ED process but also when the ZVI is used. In a consequence of carbonate scale the iron release from the ZVI might be limited or even totally blocked, when the scale surface will cover most of the iron surface. However in case of the iron generator, where anode and cathode are separated, scale does not occur on the anode surface, therefore iron release cannot be stopped totally, which is a main advantage over the ZVI. On the other hand the calcite surface on the cathode was found to be responsible for higher energy demand required for the applied voltage. The solution for this and other issues regarding implementation of the iron electro-dissolution requires development of an iron generator design and maintenance procedure.

4.3. Aeration unit

The aeration device is built from 3 main parts; distribution pipes on the top, polymer grids and a collection tank in the bottom (Figure 16). The first generation of the aerator was combined with a tray containing zero-valent iron, but in the nowadays systems the tray is replaced with separate unit as it is shown on Figure 10. When the aeration unit is put into place it contains clean and black polymer grid fillings that after some time due to the preceded iron dosage is covered by precipitated iron compounds, specifically 2-line ferrihydrite that is amorphous Fe(III) oxyhydroxide, as shown on Figure 17.

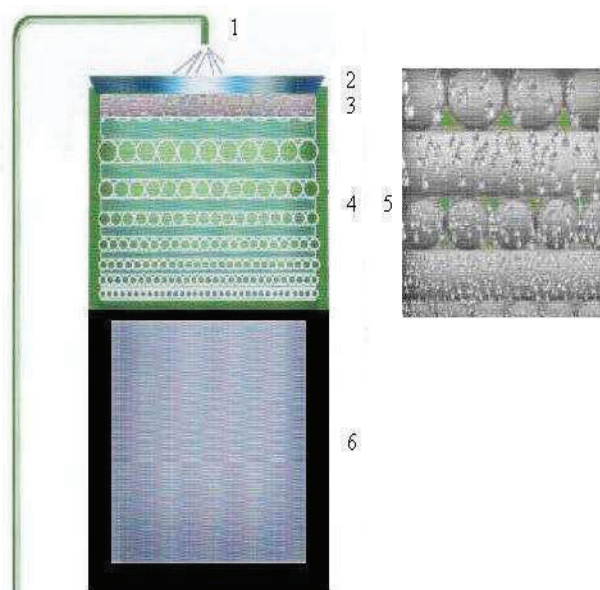


Figure 16 The general design of the MDA aeration unit (on the left): 1) inlet of groundwater; 2) distribution tray; 3) iron coil tray; 4) polymer grid pipe aeration unit; 5) polymer grid pipe oxidation unit; 6) buffer tank (Søgaard & Sønderby 2007; Lebech November 16, 2006)



Figure 17 Pictures of iron hydroxides coated (BB-FeO) and clean (BB) polymer grid pipe

The surface of ferrihydrite was found to interact with arsenic compounds during the aeration process. To understand the role of the ferrihydrite surface results from recirculation of arsenite spiked groundwater in the aeration device are shown on Figure 18. During the handling of the arsenic contaminated water changes in iron and arsenic concentration can be noticed, whereas simultaneously oxygen level and pH remain constant. It was found that the level of As(III) was decreasing in time more rapidly than it occurred in control experiments that were performed with absence of ferrihydrite coated surfaces. The decrease of arsenite in the aeration tower was found to be due to adsorption. In the pH range 6-9 As(III) is sorbed to a similar or greater

extent than As(V) to iron oxides (Dixit and Hering, 2003). However, the oxidation of arsenite on the ferrihydrite surface cannot be neglected, especially that conditions like high oxygen level and the presence of ferrous ion, might promote the transformation from arsenite to arsenate.

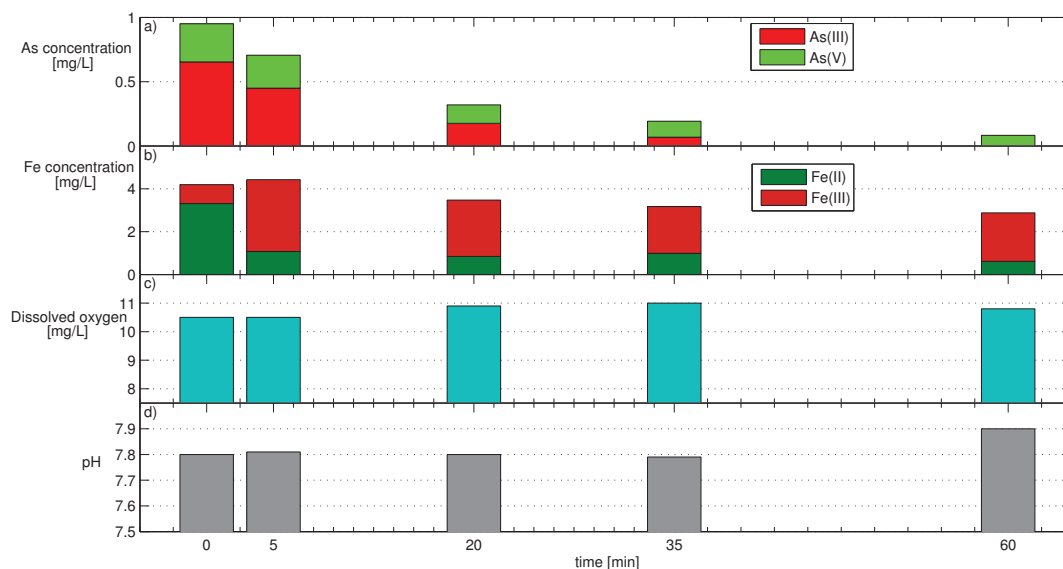


Figure 18 Results of recirculation experiment, where As-bearing groundwater was used. The values corresponds to quality of solutions sampled from the bottom tank of the aeration unit for a given time; from top: arsenic speciation, iron speciation, dissolved oxygen level and pH

The role of FeOOH coated polymer grid bodies was observed in laboratory experiments. Generally in experiments with ferrihydrite surfaces a decrease of total arsenic concentration was observed. The results clearly demonstrated that adsorption of arsenic species on ferrihydrite took place. However, in case of the iron addition the adsorption on the iron oxyhydroxide was a reversible process, contrary to what was observed in case of solely used iron oxide surface. Moreover the combination of the ferrihydrite and iron dosage resulted in the fastest arsenite oxidation and full desorption of arsenic species, which were found to be arsenate. Another phenomenon regarding the ferrihydrite surfaces is its influence on pH. The pH changes can be linked to As compound adsorption on ferrihydrite that can result in H^+ / OH^- release, as it was demonstrated in other studies (Jain et al., 1999). Therefore, making use of H^+ in complexation reactions on the surface of plastic bodies (BBFeO) might neutralize the produced H^+ that comes from arsenite oxidation.

4.4. Summary

The presented devices are an example of simple improvement of the conventional water processing. However, the implementation and design of the treatment shall consider the presence of other ions that can influence the process efficiency. For example the scale formation taking place in new iron dosage units. There are differences in scaling mechanism between the ZVI and Fe-ED favoring the second technique, due to separation of anodic and cathodic surfaces. The aeration process, and particularly a presence of ferrihydrite surface, was found to affect iron and arsenic compounds by their coprecipitation. The possible mechanisms occurring at each stage of the treatment are presented in Figure 19.

The presented processes and their combination with a separation technique can be distinguished from others technologies due to its simplicity. Therefore, the method, especially based on the ZVI may be a good option for developing countries as it can be constructed, operated, and maintained by small, not qualified communities. While application of the iron electrodisolution may fulfill the needs of waterworks in developed countries with arsenic problems.

Nevertheless, the experience from running the novel treatment in the Danish waterworks brings some insights into the system advantages and limitations regarding iron dosage method (Table 12).

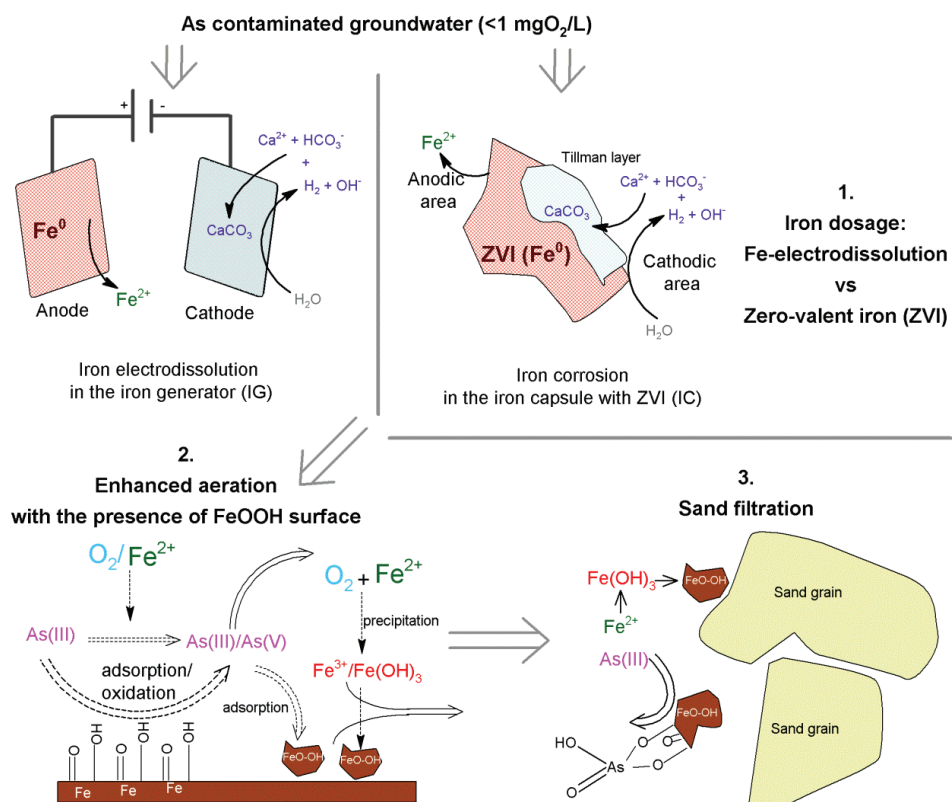


Figure 19 Possible behavior of As, Ca and Fe compounds at each step of the MDA system for arsenic removal

Table 12 Comparison of implementation of the iron capsule (ZVI) and iron generator (Fe-ED) as iron dosage methods

Parameter	Iron capsule (ZVI)	Iron generator (Fe-ED)
Costs consideration Capital expenditure – CAPEX; Operating expense – OPEX	Low CAPEX and OPEX: can be obtained from controlled scrap iron	High CAPEX - design and manufacturing of iron generator; Medium OPEX – energy for applying current; changing anode
Optimization	Not available	Current driven process, Faraday efficiency
Maintenance	Changing the ZVI source	Cleaning cathode from scale Changing the anode material
Recommended end user	Small waterworks Suitable for developing countries	Waterworks and industrial water treatment

5. Conclusions

The aim of this dissertation has been to evaluate the novel methods for improving arsenic removal for drinking water production. Based on the review of literature and the performed investigations, presented in the Papers 1 to 5, following conclusions can be drawn:

1. Arsenic presence in drinking water sources is still a major issue and application of current knowledge about these compounds can be applied for finding new techniques for water processing. A commercialization step for any novel technique shall consider technical and socio-economic aspects of the market, where it shall be delivered. The main aspects are the drinking water standards, current and future, treatment reliability and the costs.
2. The methods are a good option for decentralized waterworks, as they had been proved in small waterworks systems. Their application for long period of time revealed that it was possible to produce potable water that fulfill the Danish standards for drinking water ($< 5\mu\text{gAs/L}$). The processes were performed by help of the novel iron supplementation that was possible thanks to release of iron ions from elemental iron, but without any chemicals addition.
3. The system based on the ZVI might be suitable for developing countries replacing point-of-use methods and contributing in a better management of treatment by-products, i.e. an arsenic contaminated sludge. The proposed design of the zero-valent iron containing capsule for a long period showed that the elemental iron has been responsible for supplementation of iron ions. No interactions between arsenic and iron compounds, leading to the contaminant removal, were reported in the treatment. However, more work has to be done for optimization of the treatment regarding the iron dosage and possible biological processes.
4. The iron electrodisolution was found to be a practical method for iron dosing, where the dose depends on the applied voltage and resulting current. However improvements of the method have to be done to overcome carbonate scaling and optimize the energy consumption that can be achieved by changes in anode geometry.
5. The MDA aeration device was found to affect arsenic compounds during the treatment due to the presence of ferrihydrite surface. This surface was found to adsorb arsenite simultaneously to its oxidation. However, no proof was found that the presence of amorphous iron hydroxide enhance the oxidation rate of As(III). While the results indicate possibility of the arsenic compounds coprecipitation on the iron precipitates being initiated in the aeration unit.
6. The Fe dose was found to be a decisive factor disregarding a filtration method. The results indicate that the dose has to be raised with higher As(III) content, the presence of phosphates and natural organic matter, which were found to be responsible for hindering As removal by help of iron precipitates.
7. The conventional method, i.e. with the aeration and sand filtration, was not able to remove pesticides from groundwater. However it might be used as a pretreatment to reduce fouling potential, before application of nanofiltration or low-pressure reverse capable of removing pesticides.

6. Perspective for future work

There are numbers of advanced studies in the field of arsenic removal that focus on the new cost-effective and sustainable methods that can be applied in the developing countries. However, more valuable methods might be studies in pilot scale, where performance and expenditures can be estimated according to real case scenario. Such studies would help in applying the geochemical modeling that has been well implemented in the lab scale investigations.

The MDA system has been one of many possibilities for dealing with arsenic in the world market. However, the iron ions supplementation with help of elemental iron can be adapted to different technologies. Therefore, future studies shall focus on modeling of the iron release that takes into consideration the role of groundwater constituents and biological processes. More publications about long-term field tests will help in performing the studies.

Literature survey about amorphous iron hydroxide and some preliminary investigations indicates that the iron based removal techniques might be suitable for removal of some heavy metals from water. Therefore application of the system for removal of heavy metals from groundwater shall also be a subject of future studies.

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Removal of arsenic from contaminated groundwater with application of iron electrodisolution, aeration and sand filtration

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Abstract

The results from a new water treatment system for arsenic removal are presented. The technology is based on the employment of an electrolytic iron dissolution and efficient aeration procedure prior to sand filtration. The treatment was introduced and investigated in a pilot scale plant and full scale waterworks. The pilot scale results showed a possibility for an efficient arsenic removal from spiked solutions (with As in the range of 50-85 µg/L) depending on the process conditions (flow and applied current). In the waterworks where the system was implemented for a period of 14 months, there was a relationship where the higher applied current from the iron generator resulted in a better quality of the produced water. The long period of use also helped to determine a proper iron dosage (the Fe/As ratio 68 mg/mg) and identify carbonate scale formation in the electrochemical process. The electrolytic dissolution of the Fe was found to be a practical method for iron dosing; however more work has to be done for process improvement and optimization that shall focus on the Fe anode geometry.

Keywords

Arsenic removal, anodic iron dissolution, sand filtration, carbonate scaling

INTRODUCTION

Arsenic is a naturally occurring element in the environment, but it has proven to have negative effects on human health. In higher doses it was even originally used as a poison. Nowadays, the arsenic presence in drinking water has been shown to be responsible for diseases like vascular diseases and lung, bladder, kidney and skin cancers (United Nations 2003). Therefore the content of arsenic in drinking water is constantly monitored and its acceptable limit recommended by WHO was in 2004 reduced from 50 µg(As)/L, as established in 1984, to 10 µg(As)/L (WHO 2006). Some countries went even further and lowered the acceptable arsenic content in water below the value recommended by WHO. For example Denmark allows only 5 µg(As)/L in drinking water.

Usually, arsenic occurs in two oxidation states – As(III) and As(V). The different oxidation states of arsenic are the reason for different removal efficiencies of the As(III) and As(V) in pH range of 4-10. Trivalent arsenic molecules are in a neutral charge state as H_3AsO_3 , whereas As(V) species are negatively charged as H_2AsO_4^- or HASO_4^{2-} . The neutral charge of As(III) is the cause of inefficient As removal in some filtration processes (Parga *et al.* 2005). Conventional methods of arsenic removal are based on two processes: 1) the oxidation of As(III) to As(V), and 2) filtration of arsenic compounds (mostly As(V)). Therefore, the treatment might be based on oxidation with air or chemical oxidants, followed by coagulation and precipitation processes, where the sorption of As(V) occurs. The filtration process is most often based on arsenic co-precipitation with iron oxides that were found naturally in groundwater and enhanced arsenic removal in simple water treatments (Berg *et al.* 2006). Iron can be also dosed in different forms that enable its oxidation, if added as ferrous ion, precipitates formation that are able to adsorb arsenic via surface complex formation (Jönsson & Sherman 2008).

The application of Fe(II) instead of Fe(III) ions, which has been recently brought into focus in connection with arsenic removal, came up to have some advantages. Firstly, freshly precipitated Fe(III) (hydr)oxides, as a result of Fe(II) oxidation, hydrolysis and precipitation, were found to have a higher sorption capability than directly dosed Fe(III) compounds. Moreover, the presence of Fe(II) ions was found to increase oxidation rate of As(III) in an oxygen rich environment (Roberts *et al.* 2004, Katsoyiannis *et al.* 2008). Furthermore, an extra focus has been put on the electrolytic iron generation that is a process where direct current voltage is applied to electrodes and water acts as electrolyte (Moreno Casillas *et al.* 2007). Electrolytic iron generation is a cheap Fe(II) dosage method, especially for coagulation purposes, where it has proved its efficiency in arsenic removal (Majumder & Gupta 2011; Lacasa *et al.* 2011; Kobya *et al.* 2011). Interesting pilot studies have been described by Brewster *et al.*, where a process involving electrolytic iron addition followed by chemical oxidation with hydrogen peroxide was studied for removing heavy metals and arsenic from contaminated groundwater (Brewster & Passmore 1994). The chemical oxidant was introduced to oxidize Fe(II) and As(III). Moreover, the system required pH adjustment for creating maximum conditions for arsenate anion adsorption, which revealed a removal efficiency of 99.8%. The main drawback of this system was the relatively large amount of chemicals used for iron oxidation and pH adjustment. The addition of chemicals generates an additional cost to the treatment, which, nowadays, should be avoided or at least limited.

The primary aim of this study is to demonstrate a new treatment methodology for arsenic removal that involves an innovative use of iron electrodisolution, aeration and sand filtration. The iron dosing took place in a specially designed chamber, called an iron generator (IG), where groundwater flows during the electrolytic process. The secondary purpose of this work is to check if the iron generator enables the precise the iron dosage, which can result in specified arsenic removal efficiency. The method has been implemented in a pilot-scale treatment plant and Utterslev Kastager waterworks located in Denmark ($Q = 25'000 \text{ m}^3/\text{year}$), where it was intended to improve arsenic removal to meet Danish drinking water standards.

MATERIALS AND METHODS

Materials

The studies were performed on groundwater with low concentration of arsenic, mostly As(III) (Table 1). Additionally, the pilot plant made it possible to spike with arsenic (III) oxide (reagent grade from Sigma Aldrich, prepared by its dissolution in 1 M NaOH, VWR).

Table 1 Main features of the raw waters

Parameter	Pilot plant	Waterworks
Temperature	8±2°C	10±2°C
pH	7.3	7.4
Conductivity [$\mu\text{S}/\text{cm}$]	660	712
Organic carbon NVOc [mg/L]	1.1*	1.3*
HCO_3^- [mg/L]	373±20*	352±30*
Ca [mg/L]	50	67
Mg [mg/L]	28	18
Fe [mg/L]	0.8	0.2
As [$\mu\text{g}/\text{L}$]	8	18
	(90% AsIII)	(70% AsIII)
Dissolved oxygen [mg/L]	<1	<1

*According to the Geological Survey of Denmark and Greenland database (GEUS)

Treatment plant description

The arsenic removal treatment plant is based on the patented MicroDrop Aqua system (Søgaard & Sønderby 2007; Lebech November 16, 2006). The core of the system is an iron generator (IG) that enriches raw water with iron during electrolytic anode dissolution. The solution is aerated in the MicroDrop aeration unit containing open walled plastic tubes that like a drizzling filter increases the water-air contact surface. From the tank placed below the aeration unit, the aerated water is collected and pumped to a pressurized sand filter (quartz sand 0.2 - 1 mm). The scheme of the treatment process with the sampling taps is presented in Figure 1. The container wall of the iron generator was made from stainless steel that acted as a cathode whereas an insulated cast iron rod placed inside was acting as an anode. The area of the anode was 0.24 m² and was powered by the PS3003 Lab Power Supply with dual LCD display.

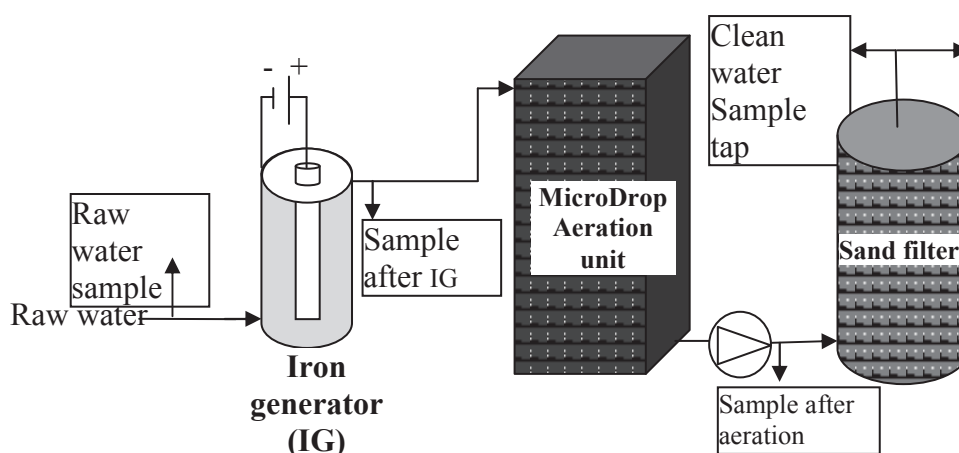


Figure 1 The scheme of the arsenic removal system, with sampling taps for samples collection

Table 2 Pilot plant vs waterworks operation procedure

	Pilot plant	Waterworks
Period of use	Short (20 min to study As removal from spiked solution, and 24 hours to study Fe release from IG)	Long (monitoring for a period of 14 months)
Sampling frequency	Once per run	Once per month
Initial As concentration	Adjustable (8 – 85 µg/L)	Fixed (18±1 µg/L)
Treated volume	1 m ³ per run (for spiked solution)	Depending on water consumption
Flow (through IG)	Different flows (0.21, 0.28, 0.30, 1.10 L/s)	Fixed flow (1.28 L/s)
Applied current	Range 0 – 3.2 A	Range 0 – 3.2 A

Experimental procedures

As the treatment was implemented at two places, with different purposes, different approaches were required. At the pilot plant, it should be possible to change the varying factors (i.e. applied current, flow and initial arsenic concentration) in short periodical tests. A tank (1 m³) was arranged to contain arsenic spiked groundwater. The time of each experiment in the pilot plant was limited by

the flow and the volume of the tank. A similar treatment system was used at the waterworks, where process efficiency depending on the applied current was monitored for a period of 14 months. The comparison of operating procedures at both sites is presented in the Table 2.

Iron generator sampling procedure

The main difficulty in monitoring the iron generator performance was collection of a representative sample. To ensure a proper sample handling the following factors had to be considered:

- Time of the response to the current change – it was found that the samples could be taken at least after 24 hours, when the electrolytic iron release with new applied current has equilibrated;
- Accumulation of the iron during the time, when water flow was paused, but current connected, caused accumulation of iron in the IG volume - at least 10 minutes after water was flowing through the IG was necessary to remove surplus iron from the IG volume.

Analysis and sample preparation

Sampling taps were placed after each unit operation within the system from each of which about 400 mL water was collected. From the primary sample 40 ml were taken for digestion with nitric acid (68%, VWR) in autoclave (30 minutes at 120° C). In case of solid samples; they were dried and the known mass, about 0.2 g, was digested in autoclave with nitric acid. The digested samples were analyzed with ICP-AES (Perkin Elmer Optima 3000 DV) for content of Fe, Ca and Mg, all with a detection limit of 0.1 mg/L. Arsenic was analyzed with hydride generation AAS (Thermo Scientific Vapour system VP100 and S Series AA Spectrometer). Additionally, dried solid samples were also collected at the Fe generator (anode and cathode surface) and from the sand filtration (sand media and backwash sludge) were examined with X-ray Powder Diffraction (XRD) on the Philips X'Pert apparatus, rad. CoK α 1. pH was measured by the Meter Lab PHM 250 pH meter (Radiometer Analytical) and dissolved oxygen was measured on-site, in the freshly collected samples, by help of OxyMeter (Oxyguard Handy MK II). Iron and arsenic speciation was determined by means of Merck photometric method no. 1.00796.0001 and filtration with use of a disposable cartridges containing aluminosilicate, accordingly.

RESULTS AND DISCUSSION

Arsenic removal performance

The physicochemical parameters were measured at each stage of the treatment, as it is indicated on Figure 1, and generally did not differ between the sites. During water processing no significant changes in pH and conductivity were observed. However, the concentrations of dissolved oxygen, iron and arsenic varied (Figure 2). The difference in concentration of iron and arsenic between outflow from iron generator and the aeration unit could have been caused by the fact that those compounds partly precipitate in the tank at the bottom of the aeration unit, where samples were collected after the each process, showing a variance. The raw water was first enriched with iron dose in the IG, which was found to be ferrous iron. This was followed by the process of aeration that saturates water with oxygen and results in a partial oxidation and precipitation of Fe(III)hydr(oxides). However, the main iron oxidation and precipitation takes place in the sand filters. Due to the high oxygen content and pH, the physicochemical mechanism of iron oxidation and precipitation is to be expected, but biological processes oxidising iron in the sand filters cannot be ruled out entirely (Davison & Seed 1983; Geroni & Sapsford 2011). Arsenic was removed by co-precipitation with the produced Fe(III) oxides and precipitation on the sand filter media (Roberts *et al.* 2004).

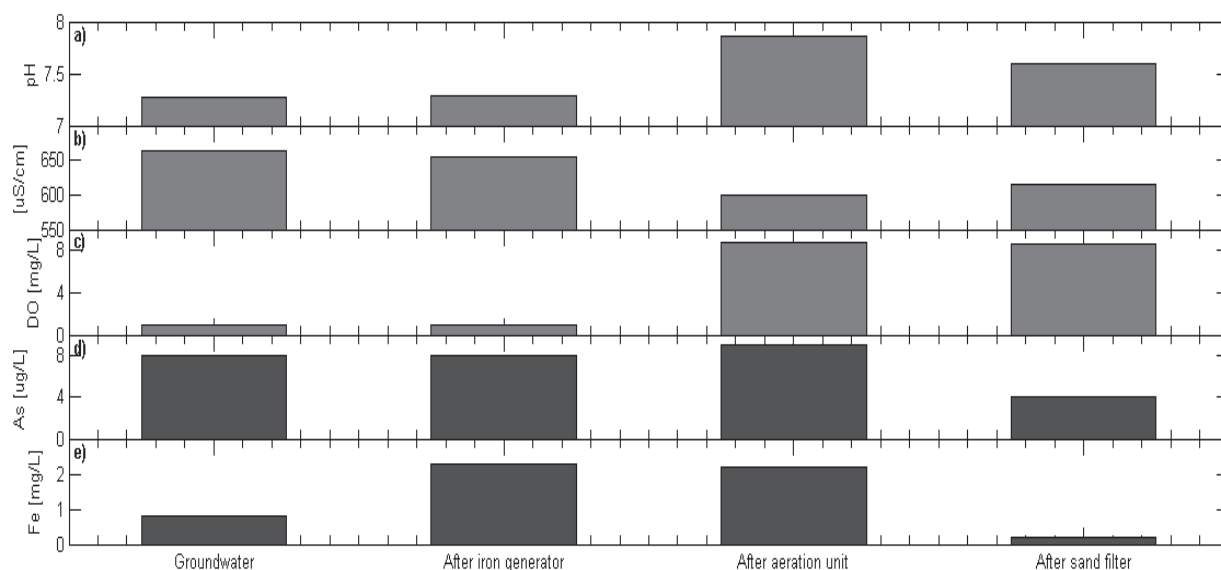


Figure 2 Water parameters at each stage of treatment during the experiments in the pilot plant (IG current of 2.1 A and flow 0.28 L/s): a) pH; b) Conductivity; c) Dissolved oxygen; d) As concentration; e) Fe concentration

Implementation of the treatment for high As concentrations was accomplished with the means of As spiked solutions used in the pilot plant. In most of the experiments with different values of flow and current, an efficient arsenic removal was observed, as it is shown in Figure 3. Noticeable is that arsenic was reduced from above 60 to 10 $\mu\text{g/L}$ when no current was applied. This, in fact, shows that the arsenic removal occurred when electrolytic iron dosage was minimized and the performance of the system was based mostly on the natural iron content of the groundwater.

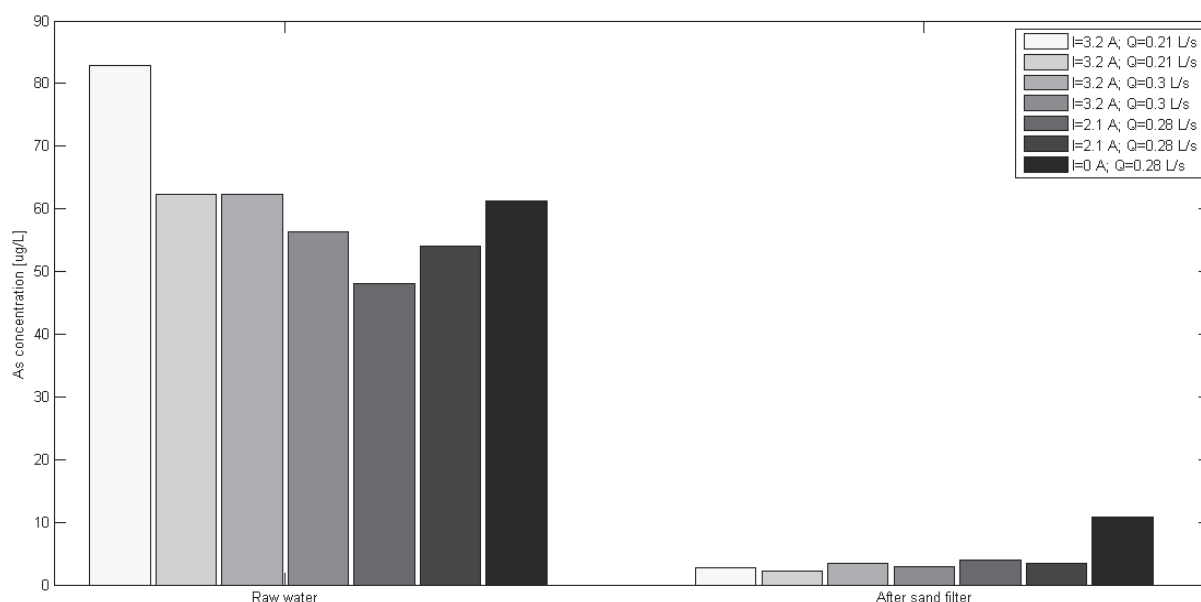


Figure 3 Results of arsenic removal in pilot plant with fixed current (I) of the iron generator and fixed flow (Q)

Long term results were obtained from the monitoring of the treatment performance at the waterworks. During 14 months of treatment the apparent response of the arsenic concentration in produced water on the applied current was observed (Figure 4). The results agree with the findings from studies about the iron electrocoagulation, where higher currents release more iron resulting in

improved arsenic removal (Amiri *et al.* 2011). The desirable concentration of 5 µg/L in produced water was achieved with one of the highest currents (3 A). The effect was observed one month after the changes in conditions were applied, but it did not last, as could be seen in the next period where arsenic slightly increased again. After 10 months of application the iron generator was purified, i.e. the stainless steel walls were cleaned for deposited residuals and the anode was shifted. Current adjustment in months 13th and 14th did not result in the same arsenic removal efficiency. However, the trend in the arsenic removal improvement when the high current was used is distinct remarkable.

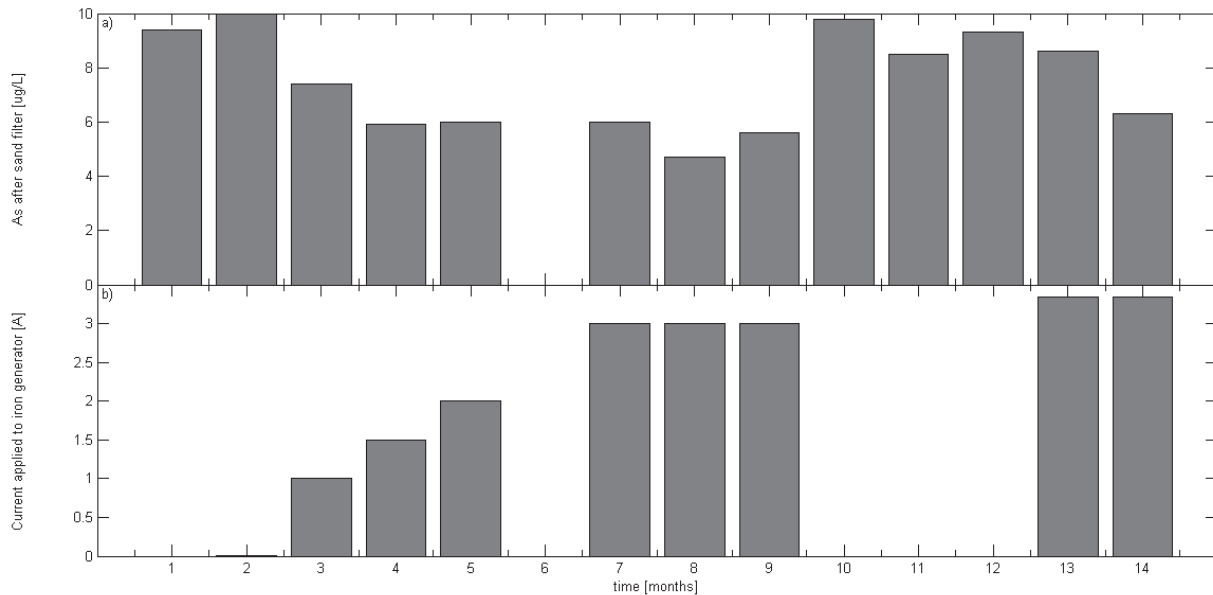


Figure 4 Response of the arsenic concentration in produced water in the waterworks (a) on the applied current in the IG (b); month 6th – sampling and reading not performed

Iron electrodisolution efficiency

It is well known that arsenic removal by co-precipitation with iron oxides depends on the amounts of iron added during the treatment (Roberts *et al.* 2004; Majumder & Gupta 2011; Kobya *et al.* 2011). Thus, the amount of iron released in electrochemical reaction is a key factor for the system description. The electrolytic process shall follow Faradays law, according to which the mass of iron released from the anode can be calculated from the following equation:

$$m_{Fe} = \frac{I \times t}{F} \times \frac{M}{Z} \quad (1)$$

m_{Fe} – mass of released iron [g]; I – current of energy source applied [A], t – time [s]; F – Faraday constant [96485 C/mol]; M – molar mass of iron [56 g/mol]; z – is the valence number of ions of the substance – in case of Fe^{2+} release it is 2.

However, in hydrodynamic conditions where water flows through the iron generator a concentration of produced iron ($C_{Fe,produced}$) will depend not only on the current (I) but also on the flow rate (Q), and the residence time (t). The combination of the factors gives the following:

$$C_{Fe,after IG} - C_{Fe,groundwater} = C_{Fe,produced} = \frac{m_{Fe}}{Q \times t} \quad (2)$$

In a simple manner the equation above describes the iron electrodisolution process in the studied system and the concentration of produced iron can be found from a difference between the Fe content in the sample before and after the IG. A mass transfer number (N), defined as the amount of iron released from the anode as a function of time, was chosen as a factor for the iron generator efficiency evaluation. The value of N can be obtained from experimental results by multiplication of the produced iron concentration [mg/L] and the flow rate [L/s]. The theoretical value of the mass

transfer can be calculated by combining Equation 1 and 2 in the following way:

$$N = C_{\text{Fe,produced}} \times Q = \frac{m_{\text{Fe}}}{t} = \frac{I \times M}{F \times Z} \quad (3)$$

The proposed factor can be used to compare the measured iron electrodisolution with the theoretical value calculated from Faradays law.

Another factor used for describing iron electrodisolution is the energy consumption which was obtained from applied current and voltage (V, volt). The energy consumption pr. m³ of water was calculated for a time of 1 hour with regard to used flow (Q, m³/h) according to following equation:

$$E = \frac{I \times V}{Q} \quad (4)$$

The efficiency of the iron generator is presented as a function of the measured to the calculated iron transfer (N), which compromise different conditions used in the pilot plant and the waterworks (Figure 5). The results from both the waterworks and the pilot plant are complementing each other, indicating that the general performance did not differ between these two sites. The iron release for I=0 could be an outlier and the result of conductivity values for the raw waters. Conductivity is related to the electrolyte resistivity that affects electrochemical process (Martínez-Villafañe *et al.* 2009). The efficiency of iron dissolution decreases with an increase of the mass transfer value N. The phenomenon might be similar to the effects reported in the studies on pure iron electrocoagulation, where it was proposed that the release of iron might be limited due to an increased diffusional resistance of Fe(II) movement near the anode surface (Kobyia *et al.* 2011). Moreover, the release of iron might be related to the anode geometry, which affects the currents distribution (Vázquez *et al.* 2012). The consequence of the electrolytic inefficiency would be an increasing amount of energy required for the iron dosage that is related to the applied current, but is only a minor part of overall energy consumption (estimated to be around 0.8 kWh/m³) (Figure 6). Nevertheless, the results of As removal where no current was applied are remarkable. This exemplifies that iron addition can probably be achieved without any energy input as the result of galvanic corrosion occurring due to the potential difference between the stainless steel cathode and the iron anode.

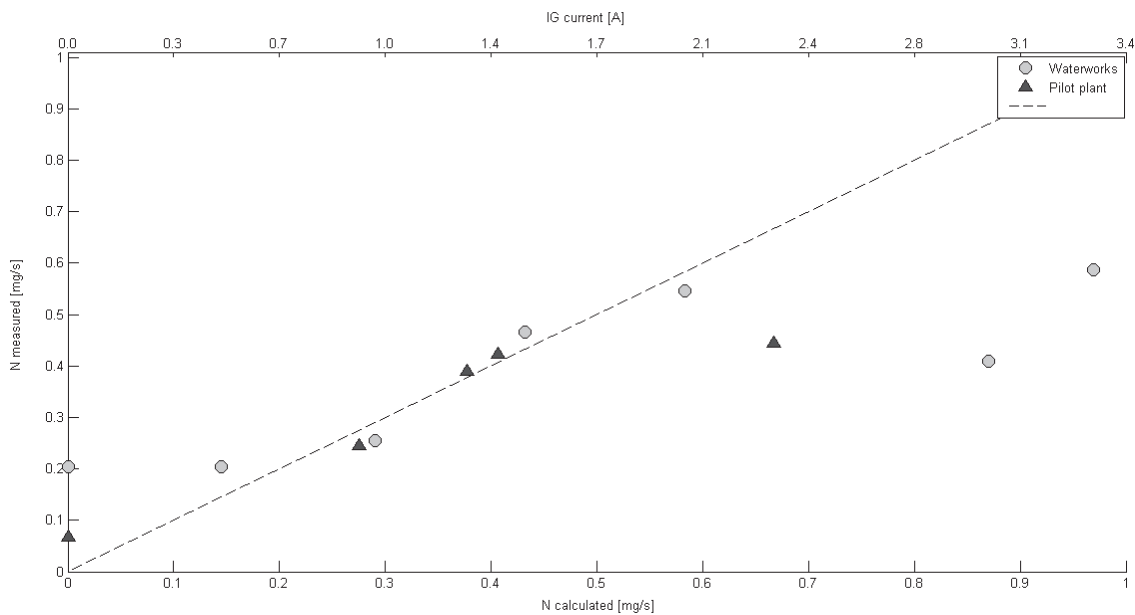


Figure 5 The efficiency of the iron electrodisolution as the function of the measured to calculated mass transfer of iron from the anode in the pilot plant (Δ) and waterworks (o) (The straight line illustrates ideal values calculated according to the Faraday law)

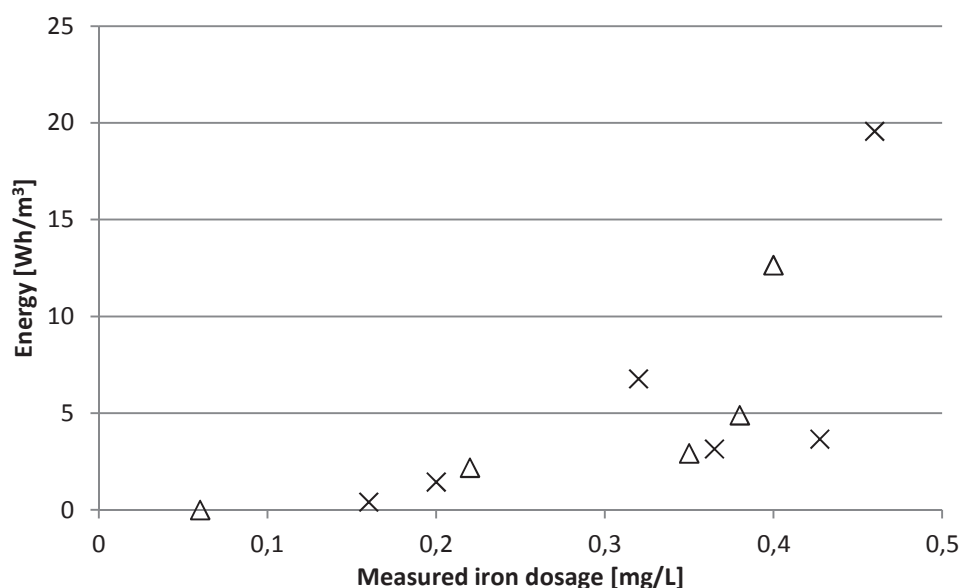


Figure 6 The energy consumption as a function of the electrolytic iron dosage measured in the pilot plant (Δ) and waterworks (X)

Analysis of the solid samples from waterworks

During maintenance of the system after 10 months a presence of solid residue on the cathode and anode in the iron generator was noticed at the waterworks. These solids were collected along with some samples of the sand filter media and backwash sludge and analyzed for metals and arsenic content (Table 3).

Table 3 Elements in the dried solid samples collected at the waterworks

	As [mg/g]	Fe [mg/g]	Mn [mg/g]	Mg [mg/g]	Ca [mg/g]	Fe/As ratio [mg/mg]
Cathode	0.03 ± 0.02	12±1	0.04±0.02	27±1	280±30	365
Anode	0.32 ± 0.02	363±2	4.6±0.4	1.8±0.4	25±4	1134
Backwash sludge	3.3 ± 0.3	225±2	0.29±0.02	3.0±0.7	65±6	68
Sand filter media	0.7±0.2	23±2	0.36±0.04	3.0±0.3	310±10	32

Beside the arsenic and iron, there were also found significant amounts of manganese, magnesium and calcium. The differences in the concentrations of the elements illustrate the fate in the waterworks treatment system. For example iron released from the anode has accumulated in the backwash sludge together with manganese that is a minor component of the anode material. Inversely, magnesium and calcium have accumulated on the cathode and were also found in the backwash sludge and sand filter media in higher concentrations than in the anode samples.

Moreover the obtained value of Fe/As ratio in the backwash sludge suggests a critical amount of iron required for arsenic removal in the treatment. The value obtained in this study is for the most part in agreement with the values reported in literature. For example, in synthesized sludge from arsenic removal by coagulation with ferric chloride an As-to-Fe ratio of 0.07-0.15 (M/M) was obtained, which corresponds to the Fe/As ratio of 5-10.60 (mg/mg) (Phenrat *et al.* 2008). This ratio is also higher than the reported sorption capacity of freshly precipitated Fe(OH)₃, which was estimated to be 15.3 mg As/g (Kim & Nriagu 2000). The freshly precipitated Fe(OH)₃ was studied

in laboratory scale experiments and this fact could be a reason for the difference in the Fe/As ratio found in this paper. The raw waters, containing organic matter as NVOC, was found to be responsible for hindering the formation of iron precipitates resulting in higher iron demand required for As removal (Rao *et al.* 2009). However, the value of the recent Fe/As ratio seems to be more related to the model that represents the amounts of Fe^{3+} necessary to attain the Bangladesh standard of 0.05 mg/L in a settlement process to remove arsenic from groundwater, that is $\text{Fe}=66\cdot\text{As}^{1.75}$ (in mg/L) (Mamtaz & Bache 2001).

Nevertheless, the Fe/As ratio indicates the level of the current that shall be applied in to achieve the desirable treatment efficiency. Thus, to remove 13 $\mu\text{g}(\text{As})/\text{L}$ (difference between the raw water and recommended guideline), it is necessary to attain an iron concentration of 0.88 mg/L, which can be reached by applying the current of 3.9 A in our reactor with a steady state flow of 1.28 L/s. This value corresponds to the observed arsenic removal efficiency in the waterworks between the 7th and 9th month of activity, when 3A of current was applied. Noticeable is the fact that the desired arsenic concentration was achieved even though the lower current was used, but an additional dose of iron was supplemented by its content in raw groundwater. However, such arsenic removal efficiency was not observed when even higher current was applied in the 13th and 14th month of testing. Although it was suspected that a measured decrease of arsenic content in produced water would continue until reaching the desirable level.

Behaviour of carbonates in iron generator

According to the calculated Langlier Saturation Index ($\text{LSI}<0$) calcium carbonate formation was not expected in groundwaters (Lenntech website 2012). The high amount of calcium and magnesium in cathode residuals can be explained by the fact that it is polarized at voltages where hydrogen is produced. The reduction reaction raises the interfacial pH sufficiently to precipitate the carbonates, which can be presented by following reactions (Barrios *et al.* 2007; Yanagisawa & Matsumura 2011):



The occurrence of calcium carbonate in the calcite form has been confirmed by the XRD analysis of the dried solid samples (Figure 7). Moreover, a presence of the magnesium led to its incorporation to the formed calcite crystals resulting in dolomite ($(\text{Ca}_{1-x}\text{Mg}_x)\text{CO}_3$), which was also confirmed by the XRD analysis (Świetlik *et al.* 2011). The results agree with observations of Gabrielli *et al.*: in case of an electrochemical scaling process at room temperature calcite was predominantly formed for conditions which were favorable to a fast nucleation rate (Gabrielli *et al.* 1999). And in the case of the iron generator it can be assumed that the favorable conditions occurred as the cathode was continuously fed with the scale-forming compounds and the current applied resulted in ensuring pH conditions, like it is shown in the reaction 1.

Additionally, with help of Matlab programming it was possible to estimate a calcite crystallite size by use of the Scherrers equation (Hammond 2009). The size was calculated for identified calcite peaks (for d-spacing: 3.035 and 2.285 pm). The results are present in Table 4. These results correspond to those obtained by Świetlik *et al.*, where size of crystallites in different water treatment plants and water intakes varied from 24 to 111 nm, depending on the magnesium to calcium ratio.

Table 4 Estimated calcite crystallite size in different residuals collected in waterworks

	Estimated size [nm]
Cathode	80±10
Sand filter media	106±9
Backwash sludge	111±5

Beside identification of calcite the XRD analysis enabled to detect a presence of a mixture of the hematite, schwertmannite and goethite in anode residuals and mixture of the schwertmannite and goethite in the backwash sludge. The presence of hematite and goethite in the anode sample can be explained by energy provided by the electrolytic process as activation energy for crystallization therefore formation of the crystalline iron minerals besides its main content of amorphous ferrihydrite. It has been shown in other studies that iron electrolytic produced is related to the production of green rust (Fe(II)-Fe(III) hydroxides) and is believed to occur also in the presented system (Moreno Casillas *et al.* 2007).

However, none of the green rust compounds were identified in the precipitates collected from the anode. The reason of that is that the samples have been in contact with oxygen from air during the sampling procedure resulting in oxidation of the original iron compounds.

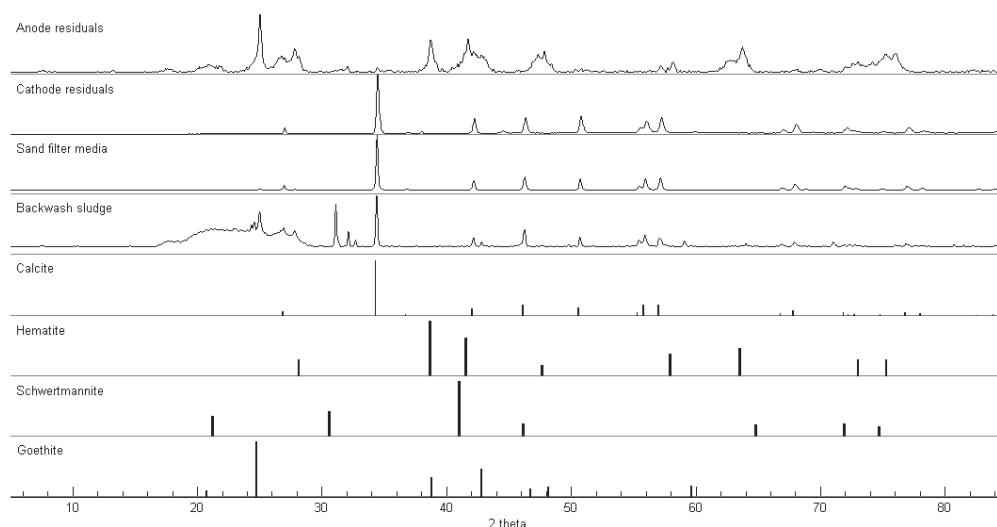


Figure 7 The XRD scans of the samples collected from different parts of waterworks treatment compared with peaks of the calcite, hematite, schwertmannite and goethite (Mindat.org website 2013)

CONCLUSIONS

It was possible to obtain arsenic removal results that follow the Danish standards for drinking water ($< 5\mu\text{g/L}$) at both test sites. The key findings from the study are following:

1. The improvement of arsenic removal efficiency showed to be corresponding to the applied current in the iron generator, thus also to the iron dosage which agrees with previous studies.
2. The iron electrodisolution method was found to be a practical method for iron dosing; however more work has to be done for process improvement and optimization that shall focus on the anode geometry.
3. The carbonate scaling was found to occur and interfere with iron release, thus affecting treatment efficiency. Therefore precautions measurements have to be taken into account for proper iron generator maintenance and a regular cleaning procedure of the iron generator shall be considered.

Finally, the presented method was able to efficiently and without any addition of chemicals eliminate trace amounts of arsenic from groundwater.

ACKNOWLEDGEMENTS

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Paper 2 (submitted)

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Paper 3 (published)

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Paper 4 (submitted)

Kowalski K., Søgaard E.G., 2014: Comparison of a sand and membrane filtration unit for drinking water production – focus on arsenic removal

Paper 5 (accepted)

K. P. Kowalski and Madsen H.T., Søgaard E.G., 2014, Comparison of sand and membrane filtration as non-chemical pretreatment strategies for pesticide removal with NF/LPRO membranes.

Water Science & Technology: Water Supply (in production)

Comparison of sand and membrane filtration as non-chemical pre-treatment strategies for pesticide removal with NF/LPRO membranes

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Abstract: Pilot plant investigations of sand and membrane filtration (MF/UF/NF/LPRO) have been performed to treat groundwater polluted with pesticides. The results show that simple treatment, with use of aeration and sand filtration or MF/UF membranes, does not remove pesticides. However, by reducing the content of key foulants, the techniques can be used as a pre-treatment for nanofiltration and low pressure reverse osmosis that has proved to be capable of removing pesticides. It was found that a lower fouling potential could be obtained by using the membranes, but that sand filter was better at removing manganese and dissolved organic matter. The results indicate that combining aeration; sand filtration and membrane techniques might be a good option for pesticide removal without any addition of chemicals and minimized membrane maintenance.

Keywords: Iron, pesticides, aeration, nanofiltration, low pressure membranes, fouling

Introduction

Membrane technologies are becoming increasingly popular due to improvements in their robustness and energy efficiency. Continuation of this trend might result in near future replacement of the well-known sand filtration technique with membrane separation. Especially, in cases where advanced treatment might be necessary to solve nowadays issues such as groundwater pollution with pesticides compounds the method will be useful. However any new approach for the water treatment has to comply with existing legislation (Danish Ministry of the Environment 2007), and Danish law limits the usage of the physico-chemical processes used in waterworks, prioritizing only simple water treatment with use of aeration and sand filtration. This strategy results in abandonment of the difficult water sources, like those polluted with pesticides, and to use those where simple treatment can be applied instead. However, there is an increasing awareness of pesticide pollution of groundwater resources used for drinking water, where the pollution has been found to be stable over a period of many years (Sogaard *et al.* 2001; Thorling *et al.* 2010). Because of the enduring pollution, it is necessary to employ a method to remove the pesticide compounds if the groundwater is to be used for drinking water. Today granular activated carbon followed by UV (GAC UV) is the preferred method for removal of pesticides in Denmark, but the use of GAC suffers from problems mainly related to saturation and foot print size (Plakas & Karabelas 2012; Sogaard & Madsen 2013).

A promising technique for removal of pesticides is nanofiltration (NF) and low pressure reverse osmosis (LPRO), which does not result in complete demineralisation and operates at lower pressures compared to reverse osmosis (Plakas & Karabelas 2012; Sogaard & Madsen 2013).
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2012). The use of NF/LPRO membranes for removal of pesticides is also favorable since it allows for a treatment that does not involve the addition of chemicals, and it can be used in a decentralized drinking water system. However, the concentrations of iron and manganese in groundwater are often high, and if they are not removed, they may precipitate and foul the NF/LPRO membrane. A pre-treatment method for iron removal could be to employ a tandem of aeration and sand filtration, which is used in the conventional treatment of groundwater. Here ferrous iron is oxidized by help of oxygen from the air and filtrated as iron(III)oxides precipitates in the sand filter (Søgaard *et al.* 2001; Pacini *et al.* 2005).

Another possibility could be replacing sand filtration with low pressure membranes such as micro- and ultrafiltration (MF/UF). It has been shown in previous studies that a combination of aeration and microfiltration, where a polymeric polyethersulfone membrane with an absolute porosity 0.2 μm was used, might be adequate for iron removal; however, it required sufficient reaction time and pH adjusted to 8 by help of sodium hydroxide (Ellis *et al.* 2000).

Another approach that has been studied is the usage of a chemical oxidant, like chlorine to enable fast and efficient iron oxidation prior to UF (Choo *et al.* 2005a). The main issue with using MF/UF membranes for filtration of rich iron solutions is that it causes significant problems with fouling, because of the iron precipitation and formation of colloidal iron. This means that the MF/UF membranes require a regular and efficient cleaning process to avoid plugging of the membrane (Soffer *et al.* 2004; Korchef *et al.* 2009). For this reason, the use of ceramic membranes could be a good option. They have higher mechanical stability compared to polymeric membranes enabling the application of high backwash pressure for fouling removal (Hofs *et al.* 2011).

In this study we evaluate conventional and membrane processes for production of drinking water from groundwater, focusing on the pesticides removal. Following the Danish policy, especially its limitations, the treatment processes were performed without any chemical reagent enhancement.

The initial experiments investigated the fate of pesticides during sand filtration and ceramic MF/UF membranes. These experiments were performed to assess whether the current technologies were capable of affecting the pesticides. The main investigations then focused on the use of sand filtration and micro-/ultrafiltration as a pre-treatment techniques for pesticide removal with NF/LPRO. The two techniques were compared with respect to removal efficiency of compounds responsible for inorganic, organic, particulate and biological fouling. Thus, permeates were examined not only for mineral and organic matter content, but also turbidity, particle size and bacteria removal were determined. Moreover, the unified membrane fouling index (Huang *et al.* 2008) was measured for each permeate since fouling indexes are a typical way of classifying the fouling potential of a given water source.

Materials and Methods

Water characterization

The experiments were performed with use of natural groundwater that was acquired from an abandoned drinking water well in Vognsbølparken, Esbjerg, Denmark. Composition of the groundwater can be seen in the Table 1. For investigation of manganese and pesticides, the raw groundwater was spiked with manganese (II) ions in form of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, Sigma Aldrich and a mixture of pesticide that contained atrazine (Pestanal, Fluka), atrazine- d_5 (Pestanal, Fluka), bentazon (Pestanal, Fluka),

2,6-dichlorobenzamide (BAM) (Pestanal, Fluka) and desethyl-desisopropyl-atrazin (DEIA) (Pestanal, Fluka). All pesticides were purchased at Sigma-Aldrich. Methanol and acetonitrile (HPLC grade) and acetone were purchased from VWR. Demineralised water was produced in house with a Silex II ion exchanger from SILHORKO.

Table 1 Composition of raw groundwater taken from pilot plant for membrane filtration

Parameter	Raw
pH	6.6-6.8
Turbidity[NTU]	3.0-4.0
O ₂ [mg/L]	<0,5
Fe total [mg/L]	3.5-4.2
	90-100
Fe (II) [% of total Fe]	
Ca [mg/L]	35
Mg [mg/L]	3.6
Cl ⁻ [mg/L]	35
SO ₄ ²⁻ [mg/L]	2
UV[Abs at 254 nm]	0.35±0.05

Aeration and sand filtration method

For the investigation of the aeration and sand filtration process, a pilot plant installed at the well site was used. The plant is shown in Figure 1. Aeration was performed with MicroDrop Aqua aeration unit containing open walled cylindrical plastic tubes that like a drizzling filter increases water-air contact surface. For sand filtration a pressurized filter (1m³ of quartz sand 0.2-1 mm) was used.

Two procedures were used: continuous flow of groundwater through the system, and recirculation of a groundwater batch. The first procedure was used to evaluate the iron and spiked manganese (reaching a concentration of 1,2 mg/L in feed water) removal and turbidity lowering, while the second procedure was used to evaluate the effect on pesticides. In the recirculation procedure 120 L of groundwater was collected in a holding tank where it was spiked with pesticides to obtain a concentration of 2 µg/L. This concentration value was chosen to avoid the pesticides having an effect on the microorganisms in the sand filter, and to avoid saturation. If the pesticides adsorb to the sand filter, saturation may be reached quickly by use of higher concentrations and hereby hide the adsorption effect. Also concentrations in this range are close to what is found in real polluted groundwater. The spiked solution was then allowed to recirculate for 15 minutes for homogenisation. Before each experiment, water was allowed to run through the system for 30 minutes to obtain fresh groundwater. Triplicate samples of 1 L were taken at three places: before aeration, after aeration and after sand filter. For each sample pH and dissolved oxygen was measured.

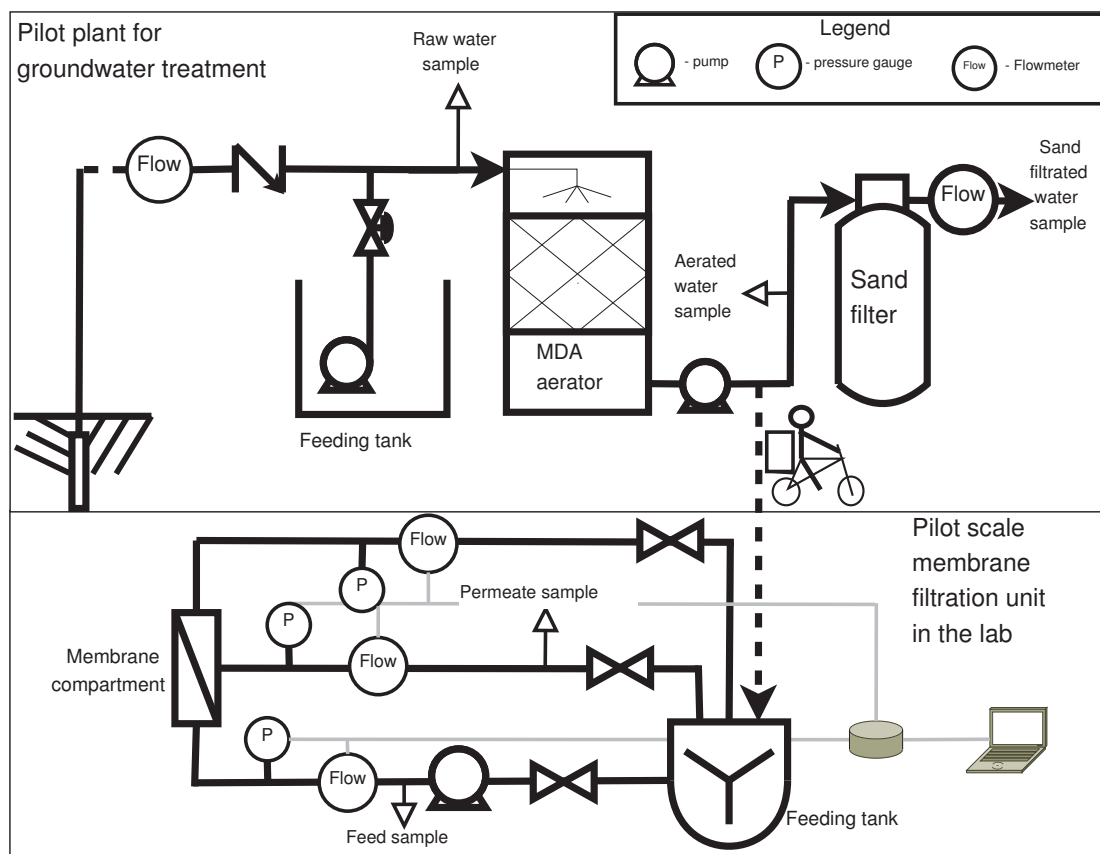


Figure 1 Pilot plant scheme for groundwater treatment

Aeration and MF/UF method

MF/UF membrane filtration was carried out with four silicon carbide ceramic MF/UF membranes with reported pore sizes: 3, 1, 0.1 and 0.04 μm from CoMeTas (now LiqTech) – system shown on the Figure 1. The membranes differs in surface area and geometry; i.e. membranes with pores sizes of 3 and 1 μm membrane had area of 0.09 m^2 and 31 channels and those with pores sizes of 0.1 and 0.04 μm had area of 0.05 m^2 and 19 channels.

For experimental purposes 100 L of aerated groundwater was collected at the pilot plant and transported to the membrane filtration unit. Pesticide removal was investigated by spiking pesticide mixture to the feed water to obtain a concentration of 2 $\mu\text{g/L}$, and the filtration was performed for each membrane separately with a transmembrane pressure between 200 and 300 mbar in a recirculated cross-flow mode. Two samples of 400 mL were taken from the feed, retentate and the permeate. Flow and pressure were measured for each stream, and was used to monitor the degree of fouling on the membranes. To clean the membranes, a 3 bar back flush was used. To evaluate the efficiency of the filtration, particle size distribution was determined before and after filtration.

Nanofiltration method

Nanofiltration and low pressure osmoses were investigated with a DDS Lab-Unit 20 equipped with two commercial membranes: NF 99 HF from Alfa Laval, Nakskov, Denmark and NF90 from Dow chemicals. The NF99HF is a classic NF membrane that shows selective removal of divalent ions, whereas the NF90 membrane is characterized as a tight NF membrane, which might also be classified as a LPRO membrane. The nanofiltration experiments were conducted by first recirculating

distilled water through the system for 30 minutes at 10 bars to clean and compress the membranes. Then the distilled water was replaced by 4 L of pesticide solution with 1 mg/L concentration. Concentrations of 1 mg/L were chosen to avoid solid phase extraction as a preanalytical method and thereby increase the variance of the results. The use of pesticide concentrations of this value is standard in membrane filtration experiments and is not expected to influence the true rejection. Before samples were collected, the filtration system was allowed to run for one hour to ensure that adsorption to membranes and equipment would not influence the results. After the one hour of recirculation triplicate samples were extracted over a 10 minute period and transferred directly to vials for analysis. The filtration was run at 25 °C, 10 bars, flow of 8 L/min and a total membrane area of 59 cm². Because only small samples were extracted, the recovery was low and the concentration of the solution would not affect rejection.

Analytical methods

From the primary sample were taken 40 mL for sample digestion together with nitric acid in an autoclave (30 minutes at 120° C). The prepared samples were analyzed by use of the ICP-AES (Perkin Elmer Optima 3000 DV) for content of Fe, Mn, Ca and Mg all with a detection limit of 0.1 mg/L.

Pesticides were analysed with a SPE HPLC/ESI-MS method. The procedure for the solid phase extraction was: activation of column with 6 mL methanol, equilibration with 6 mL of demineralized water, application of 500 mL of sample on column, elution of interferences with 6 mL demineralized water, vacuum drying of column for 30 minutes, elution of analytes with 10 mL acetone, evaporation of acetone at 70 °C and dissolution in 0.5 mL acetonitrile spiked with 0.1 mg/L internal standard (atrazine-d₅). For solid phase extraction, TELOS ENV 200 mg/6 mL was used. The HPLC method was specific for each pesticide. For atrazine, BAM and bentazon an eluent of methanol (A) and 5 mM ammonium acetate pH 3, adjusted with formic acid (B) was used, while for DEIA the pH was set to 6.5. For atrazine, BAM and DEIA an eluent mixture of 70/30 A/B was used, while for bentazon a 65/35 mixture was used. A ZORBAX Eclipse Plus C18, 3.5 µm, column was used. On the ESI-MS, the nebuliser pressure was set at 40 psi, the nebuliser flow at 9 L/min and the dry temperature at 350 °C.

pH was measured by Meter Lab PHM 250 pH meter (Radiometer Analytical) and Oxygen with OxyMeter (Oxyguard Handy MK II) in the freshly collected samples. The Merck photometric methods were implemented to determine the following: iron speciation (Fe(II) and Fe total) with method no. 1.00796.0001, chloride ions with method no. 1.14730.0001 and sulphate with method no. 1.14548.0001. Turbidity was measured with the compact AQUALYTIC® infrared turbidity meter.

Particle size was determined by help of a PhotoCor dynamic light scattering (DLS) instrument that was used to gather light scattering data. Bacteria count was performed according to the Danish Standard 2251:1983, where collected sterile samples were cultivated for 7 days with agar (DS 2251:1983 1983-01-01).

Unified membrane fouling index

To obtain an overall indication of the effectiveness of sand filtration and MF/UF membranes for reducing the fouling potential, the unified membrane fouling index (UMFI), based on Hermia's model (Huang *et al.* 2008), was applied. In this model fouling is often assumed to be purely due to cake filtration, in which case the UMFI can be obtained from the slope of a linear relationship between experimentally obtained specific flux, J'_s , and cumulative permeate volume, V_s :

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$$\frac{1}{J'_s} = 1 + (\text{UMFI})V_s$$

Where J'_s is dimensionless normalized specific flux, equal to $1/\text{TMP}'$ and TMP' is normalized transmembrane pressure $\text{TMP}_t/\text{TMP}_0$; V_s is the permeate throughput defined as the cumulative volume of permeate per membrane surface area (L/m^2). The model was applied for constant pressure (2 bar) dead-end filtration test using a 0.04 μm cellulose filter with area of 0.00096 m^2 .

Results and discussion

Removal of pesticides

Based on the pore size of sand filters and MF/UF membranes, they are not expected to be able to remove pesticides. However, several factors could influence the fate of pesticides through these processes and hereby affect the level of pesticides. It is possible that some of the pesticides are removed together with the iron oxides. This could happen through adsorption to the iron oxide colloids, which would lead to co-precipitation of the pesticides. Another possibility is that the enhanced aeration by help of the MicroDrop system could lead to stripping off some of the pesticides, especially the smaller ones such as DEIA and BAM, similar as it is known to occur for smaller chlorinated solvents. Finally, it could be possible that the microorganisms in the sand filter would be able to metabolize some of the pesticides.

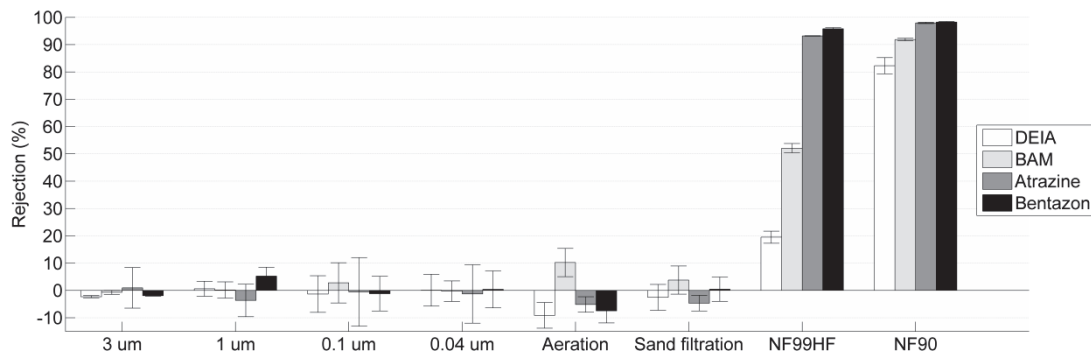


Figure 2 Comparison of the removal of pesticides by ceramic MF/UF, aeration, sand filtration and NF/LPRO membranes. Data points represent the average of the collected samples plotted with error bars indicating the standard deviation of the measurements.

As seen in figure 2, no change in pesticide concentration was observed during aeration, sand filtration or the MF/UF membranes. The observed differences are explained by the combined variance of the sampling, SPE and instrumental procedure. Neither sand filtration nor MF/UF processes can as such be expected to affect pesticide concentrations. Instead the two polymeric membranes were found to be capable of removing the pesticides. For the two larger pesticides, atrazine and bentazon, the NF membrane is sufficient, whereas to remove the two smaller pesticides, BAM and DEIA, a tight NF or LPRO membrane is necessary. The results show that in a removal procedure of pesticides in water, sand filtration and/or MF/UF membranes are better used as pre-treatment techniques to the NF/LPRO processes.

Pre-treatment of groundwater

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To evaluate the suitability of the four ceramic membranes and the sand filtration process as pre-treatment techniques for subsequent NF/LPRO, they were compared on their ability to reduce inorganic, organic, particulate and biological fouling potentials. Properties of groundwater samples collected before and after the different processes are presented in the Figure 3. For filtration purposes aerated groundwater was used, where DO content was higher (9.5 mg/L) resulting in differences between values of some factors from raw groundwater presented in Table 1.

With respect to the inorganic fouling potential, the sand filter and the ceramic membranes were evaluated on their ability to remove iron and manganese. Concerning the removal of iron, the sand filter is found to outperform the two MF membranes, while the UF membranes are able to remove slightly more iron than the sand filter. None of the membranes were found to remove manganese, but the sand filter was found to reduce it from 1.2 to 0.06 mg/L. This points at a difference in the removal mechanism for the two pre-treatment methods. Membrane filtration operates in the principle of size exclusion, and as such it was anticipated that iron removal efficiency would be correlated with membranes pore size. Unexpectedly, MF with 3 µm pore size was found to give higher iron removal than MF with 1 µm pore size. This finding was confirmed in several repeated experiments with two different membrane units of the same type. It is possible that the pore size reported by the producer was not correct, which would explain why the 3 µm membrane was found to be consistently better on all parameters compared to the 1 µm membrane. Other possible explanations could also be internal pore blocking of the 3 µm membrane or difference in the pore size distribution of the two membranes. The specific underlying reason was not investigated in this study. Removal of iron and manganese in a sand filter is based on precipitations rather than size exclusion. Sand filtration enables autocatalytic processes involving precipitated iron hydroxides on the sand media surfaces, which results in much faster iron oxidation and precipitation compared to its rate of oxidation in an aerated water solution of iron(II) (Davison & Seed 1983; Geroni & Sapsford 2011). Furthermore, the effect of naturally occurring iron and manganese oxidising bacteria cannot be neglected. For example by help of the iron oxidizing bacteria *Gallionella ferruginea* that was also found to grew uninhibited and perform biological iron oxidation in partly oxygen-saturated natural water in circum-neutral pH range (Søgaard *et al.* 2001; Pacini *et al.* 2005; de Vet *et al.* 2011). The fact that a large part of the oxidation of iron and manganese occurs in the sand filter, gives the sand filter an advantage over membrane filtration, that require pre-oxidation and particulate matter formation to occur prior to filtration (Ellis *et al.* 2000).

The fouling potential of organic matter was evaluated by measuring the UV absorption at 254 nm. Here the sand filter was found to result in a higher removal level compared to all four membranes, which were found to give equal removals. The fact that the membranes give the same content of organic matter in their permeates indicates that the organic compounds that permeates are smaller than the pore size of the membranes. The removal of NOM in the sand filter could be because of biological activity, where microorganisms are capable of metabolizing part of the organic matter. Moreover, the diverse efficiency of iron removal could have impacted organic matter removal, as it was suggested in other studies indicating that the precipitated iron can play a part in removing NOM from water by sorption (Choo *et al.* 2005b).

The two ceramic UF membranes were found to give the highest reduction in turbidity, while the sand filter gave a slightly higher reduction compared to the MF membranes. When comparing the average particle size, it is seen that the smallest particles are found in the sand filter permeate. The difference between turbidity and particle size

performance, even though the fact that the both factors refer to particulate matter, might be caused by the fact that the dynamic light scattering device (DLS) measures average particle size and not their quantity. Moreover, iron removal efficiency corresponds to the particle size found in permeates, which suggest that the colloidal iron was an important part of particle size results.

To assess the biological fouling potential, the number of colony forming units (CFUs) was measured before and after filtration. The membranes gave higher reductions in the number of CFUs compared to the sand filter, but none of them were found to completely remove the microorganisms in the groundwater. This is a clear indication of that the labelled pore sizes of these membranes may not be correct, or that the pore size distribution is relatively large since membranes with pore sizes below 0.2 μm should ensure a complete removal of CFUs (Bobbitt & Betts 1992; Hofs *et al.* 2011). In a previous study, the pore size of the used 0.04 μm membrane was determined with porometry to be 0.96 μm (Hofs *et al.* 2011). In general though, membranes will be better than sand filters at reducing biological fouling. The sand filter is in part a biological process, and microorganisms from the sand filter may detach from the sand filter, and end up in the permeate.

The unified membrane fouling index (UMFI) ranged from 0.07 m^{-1} for the 0.04 μm permeate to 1.0 m^{-1} for the sand filter permeate. The UMFI was obtained for permeates from experiments with a Mn-spiked solution. The difference between UMFI values seems to be correlated to the CFU counts and the turbidity, which indicates that biological and particulate fouling are the main causes of the measured UMFI values.

The UMFI values may be considered as the overall indicator of the fouling potential, and based on these values, the 0.04 μm should be considered as the best pre-treatment method. However, this view may be too simplified. The analyses show that the sand filter and the membranes both have strengths and weaknesses. The sand filter is good at removing iron, manganese and organic matter, but ineffective in removal of particulate and biological matter. The membranes can obtain high removals of iron, particles and microorganisms, but dissolved matter and particles below the pore size of the membranes will not be removed. This should be considered when choosing a pre-treatment strategy. If the groundwater is low in organic matter and manganese, aeration and a UF membrane system will be sufficient, but if the content of dissolved organic matter and manganese is high, a combination of aeration, sand filtration and UF membranes may be the best choice for a pre-treatment strategy.

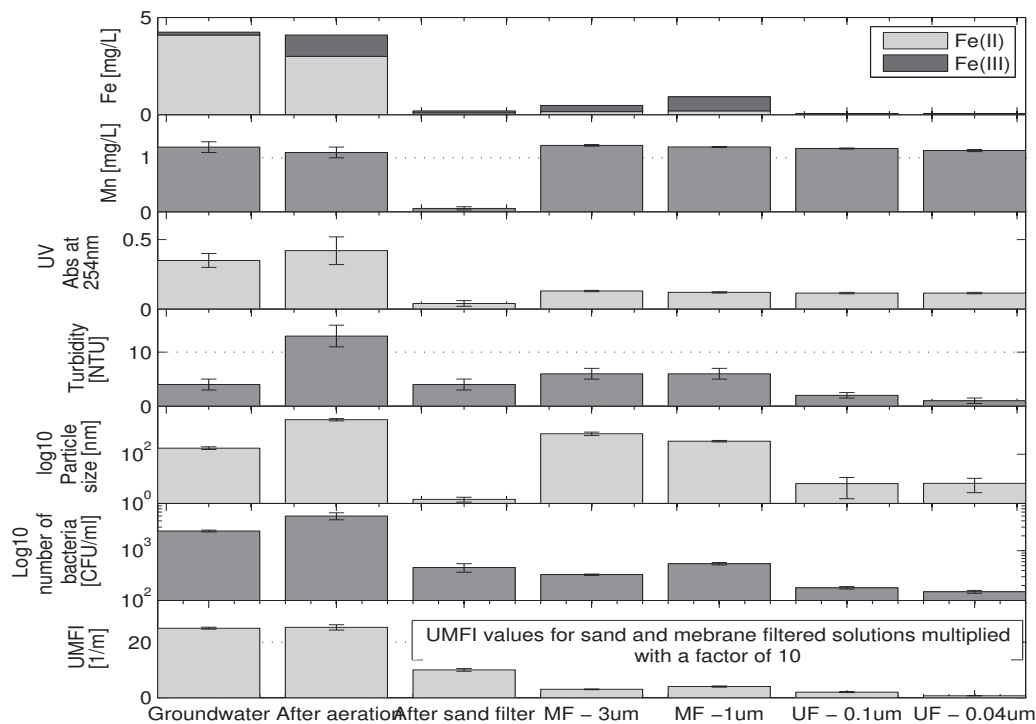


Figure 3 Quality of effluents collected after different stage of groundwater treatment (presented results for solution after aeration correspond to feed water used in MF and UF); Membrane filtration was performed with TMP of 200 mbar in cross-flow mode, Values are averages of the collected samples and the error bars represents the variance of the measurements from duplicate samples collected from the same experimental set.

Conclusion

Aeration and sand filtration/MF/UF membranes were found to be unable of removing pesticides from polluted groundwater, and these techniques should instead be used as pre-treatment methods for subsequent NF/LPRO treatments. Sand filtration was found to be effective at removing iron, manganese and dissolved organic matter, whereas its effect on particulate and biological matter was found to be limited. Ceramic UF membranes were found to be effective at removing iron, particulate and biological matter, but unable to remove manganese and dissolved organic matter.

The results indicate that the main cause of fouling in groundwater might be iron, biological and particulate matter that was found to be correlated with the UMFI of sand filtrated permeate.

The lowest UMFI was obtained by the use of the UF membrane with the smallest pore size (0.04 µm) used in this study, and is the most promising pre-treatment technique. However, in cases with high concentrations of dissolved organic matter and manganese, a serial combination of aeration, sand filtration and ultrafiltration may be the best choice.

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